Hydrodynamics of ferronematics and ferrogels

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Summary of the thesis

Some 30 years ago the idea was born to mix nano-sized magnetic particles with nematic liquid crystals, in order to get fluids with a large magnetic susceptibility. Quite recently stable and well defined systems have been produced and it became evident that these emulsions are interesting materials not only because of their enhanced magnetic susceptibility. This thesis studies systematically the new, mainly dynamic, features of such ferronematics. It makes a number of theoretical predictions for qualitatively new effects that can be tested experimentally. The method used is that of phenomenological hydrodynamics and its extension to slowly relaxing, non-hydrodynamic variables. This is a well established method to get a reliable set of (partial differential) equations that describe the long wavelength and low frequency behavior of complex fluids and soft matter. It is phenomenological in the sense that parameters (susceptibilities and transport coefficients) are introduced, whose magnitude is not known a priori. Emphasis is laid, thus, on qualitatively new effects.

First, the possible phase structure of these materials has been investigated. Conventional ferrofluids do not show any phase transition and are "super"-paramagnetic at any temperature, particle concentration, or density and no transition. That means, there is a large (saturation) magnetization even for moderate or low external field strengths. No ferromagnetic state with a spontaneous magnetization has been observed. Ordinary nematic liquid crystals show a transition from an isotropic state to the nematic state (with orientational order) at a certain temperature (thermotropic) or concentration (lyotropic) in the case of solutions. The question was, what kind of phase transitions are possible in ferronematics with respect to both, nematic (orientational) and magnetic (ferromagnetic) order. Within a simple Landau free energy description up to fourth order in the appropriate order parameters it could be shown that there are two different ferronematic phases (apart from an isotropic one at high temperature or low concentration): one with nematic but no magnetic order (superparamagnetic) and one with both types of order. Within this model a phase with magnetic but no nematic order seems to be impossible. The transition from the isotropic to the ferromagnetic phase can be either directly or in two steps via the (super)paramagnetic nematic phase. Those transitions, where the nematic order is built, are always first order. In the presence of an external magnetic field the transitions are smeared out and at high fields can become second order. In an external magnetic field the behavior of a superparamagnetic and ferromagnetic phase are rather similar. Up to now no clear experimental evidence for a ferromagnetic phase has been found, but experiments at low or vanishing fields are rather scarce.

In a second step the macroscopic dynamics of (superparamagnetic) ferronematics has been explored. Generally, one has to consider the dynamics of the nematic degree of freedom (reorientation of the preferred direction in space) as well as the magnetic one (rotations and size changes of the magnetization). Since the latter usually is much faster than the former, one can consider the special case that the magnetization has already relaxed to its equilibrium value and direction (set by the external field). Then a ferronematic dynamics has the same structure as that of a conventional nematic liquid crystal. Only the static and dynamic response to external fields is much stronger. In conventional nematics the influence of a magnetic field on the dynamics had been neglected or not considered at all, previously. Here such dynamic effects

are studied systematically. They can be linear in the external field, in contrast to the static (superparamagnetic) effect, which has to be quadratic in the field due to time reversal invariance (of the free energy). In the dynamics, currents can be odd or even under time reversal, so describing reversible or irreversible behavior. Thus, the new linear dynamic field effects always toggle between reversible and irreversible, when compared to their non-magnetic counter parts. Among the effects discussed are reversible ("Hall'-like) contributions to heat, concentration, and thermodiffusion currents as well as viscosity and director relaxation, and an irreversible contribution to flow alignment effect. The latter is manifest in a shear flow experiment, with the magnetic field in the shear plane, where in a ferronematic the nematic director orients with a non-vanishing component out of the shear plane, while in conventional nematics the director orients in the shear plane. Another testable effect of a new linear dynamic effect is the relaxation of the director into a direction set by an external magnetic field. For conventional nematics this is a simple relaxation process, where the director and the magnetic field lie always in the same plane. In ferronematics an oscillation is superimposed on the relaxation connected with a spatial wobble.

In the more general case the dynamics of the magnetization has to be taken into account. Since the director can be either parallel or perpendicular to the field (and the magnetization) in equilibrium, there is a uniaxial and a biaxial case. The third possible case that the director, the magnetization and the magnetic field are all pointing in different directions, but lie in the same plane, is disregarded here, since it has not been found in experiment yet. The dynamics is rather rich: In addition to the coupling of the orientational changes of the magnetization and the nematic director reorientations, there are reversible and dissipative dynamic cross-couplings of compressional, shear and elongational flow with rotations and changes of the absolute value of the magnetization and director reorientations. For measuring some combinations of the parameters that describe these cross-couplings we studied the sound wave spectrum and the rheology of shear flow. In particular the sound spectrum is studied and a field-dependent contribution to damping is found. Additionally sound waves (compressional flow) can trigger shear flow (and vice versa), if the wave vector is oblique to the field direction. Oscillatory shear (without field, or with a field parallel or perpendicular to the wave vector) shows a considerable influence of the magnetic degree of freedom. Even without a magnetic field the apparent viscosity is different from the bare one and the modified nematic director diffusion couples to the flow response. In the presence of an external field the director relaxation is shifted to a finite frequency, which approximately increases with the third power of the field strength.

Finally the dynamics of ferrogels is investigated. Here the magnetic particles are put into a matrix of cross-linked polymers. Ferrogels can be isotropic or uniaxial depending whether the cross-linking process is done with or without a magnetic field, although we only deal with the former one. An external field leads to a static deformation of the gel (magnetostriction). The dynamic around this strained equilibrium state shows various peculiar features. The dynamic coupling of the magnetic degree of freedom to the elastic one leads to magnetic field dependent effective (longitudinal and transverse) sound velocities. The dispersion relations show characteristic steps at the frequency of the magnetization relaxation. This frequency and field dependence of the sound spectra, thus provides the opportunity to measure the relevant static and dynamic magneto-elastic parameters that are crucial for the possible applications of ferrogels.

Contents

Chapter 1

Introduction

1.1 Ferronematics

Ferrofluids are suspensions of nano-sized ferromagnetic particles in some carrier liquid (for example, water or oil) [1]. Without an applied external magnetic field the orientations of the magnetic moments of the particles are random resulting in a vanishing macroscopic magnetization (magnetic disorder). An external magnetic field, however, easily orients the particles' magnetic moments and a large (induced) magnetization is obtained. This "superparamagnetic" property is the basis for many applications.

In 1970 the idea emerged [2] to dope nematic liquid crystals with a small amount of ferromagnetic grains (volume fraction of $10^{-5} - 10^{-4}$) in order to enhance the magnetic susceptibility. The expectation was that a strong coupling between the orientation of the magnetic grains and the nematic ordering induces a spontaneous macroscopic magnetization (ferromagnetic state), which allows easy control of the director alignment by weak external magnetic fields.

Quite rapidly, mixtures of thermotropic calamitic [3, 4] and discotic [5], as well as lyotropic nematics [6] with ferroparticles were produced. However, these systems were more like dirty liquid crystals, where the magnetic additives served for a better orientation of the nematics in an external field. Problems were the stability of these mixtures and the mutual orientation of the director and the magnetization. The experimental situation changed considerably, when it was possible to make stable emulsions, first as ferrosmectic systems [7–9], were the ferromagnetic nano-particles are embedded in the layers. These ferrosmectics are very dilute systems, which prevents their use in applications. Recently, stable ferronematic systems, where the liquid crystal and the magnetic aspects are on equal footing, have drawn increasing attention (apart from other rather exotic phases, like ferrovesicles [10]). Birefringence [11–13] behavior in homogeneous electric [14], and magnetic fields (including the Frederiks transition [11, 15–17]) in inhomogeneous fields [18], and under the influence of bounding surfaces [19] have been investigated.

In their original work Brochard and de Gennes started from the so-called "rigid anchoring" approximation, implying that the directions of the director $\mathbf{n}$ and the local magnetization $\mathbf{M}$ are perfectly co-aligned. However, with the synthesis of thermotropic ferronematics [20] it became evident that the rigid-anchoring approximation might not be generally applicable. Within the framework of a microscopic model of rod-like ferromagnetic grains Burylov and Raikher [11] reconsidered the surface interaction between the liquid crystalline nematogens and

derived an expression for the free energy of a ferronematic. Thereby the orientations of $\mathbf{n}$ and $\mathbf{M}$ were treated as separate degrees of freedom. As in Ref. [2] the strength of the magnetization was assumed to be in saturation, even without external fields. However, the existence of a remanence in ferronematics, being characteristic for a ferromagnetic ordering (spontaneous equilibrium-magnetization in the absence of any external magnetic field) seems to be experimentally unproven yet. Rather the existing substances all seem to be superparamagnetic like ordinary ferrofluids.

1.2 Ferrogels

Ferrogels belong to a new class of magneto-controlled elastic materials, which are chemically cross-linked polymer networks swollen with a ferrofluid. Coupling the elastic medium with the magnetic properties of the particles allows to manipulate the elastic behavior of ferrogels by external magnetic fields. This feature offers opportunities for various applications as e.g. soft actuators, micromanipulators, and artificial muscles [21]. Heating of these materials in alternating magnetic fields allows for a promising approach in cancer therapy [22]. Since the magnetic rubber is soft, inexpensive and controlled by the magnetic field, it can also be used in an apparatus for immunoblotting [23].

The properties of ferrogels depend on the preparation conditions (solvent, concentration of cross-linking, concentration of magnetic particles). Preparing ferrogels in an external magnetic field one can obtain large columns of magnetic particles, the size of which is much larger than the mesh size of network. In this case the clusters are fixed in the network [24]. As a result the ferrogel is strongly anisotropic [25].

Here we consider isotropic ferrogels. The typical size of the magnetic particles is ~ 10 nm. The bare particles tend to coagulate. To prevent this, magnetic grains are charged [17] or coated by polymers [26]. The magnetic gels are usually only weakly cross-linked, so that the size of the magnetic particles is much smaller than the mesh size of the network. However, still some coagulation takes place resulting in magnetic clusters comparable in size to that of the mesh [27]. Without external field no remnant magnetization is found. An external field easily magnetizes the sample (superparamagnetism). Outside equilibrium the magnetization relaxes to its equilibrium value and orientation set by the external field. This relaxation is rather slow compared to the (many) microscopic relaxation processes.

In inhomogeneous magnetic fields an abrupt shape transition of isotropic ferrogels was observed [27]. The force generated by such a magnetic gradient field drives the magnetic grains in the direction of the gradient, thus deforming the network, if there is a coupling between the magnetic particles and the network. In these experiments this seems to be the case.

1.3 Scope of this thesis

In chapter 2 a Landau-type free energy function is presented to describe the phase transitions from an isotropic (superparamagnetic) ferrofluid to a ferromagnetic nematic liquid crystal either directly or via a superparamagnetic nematic liquid crystal. These two nematic phases are usually both called 'ferronematic', although they are distinct phases. Both show nematic ordering, but only the ferromagnetic phase shows spontaneous magnetic ordering, additionally.

The interplay of nematic with magnetic order is of special interest. A phase with ferromagnetic order but no nematic order is not possible in the present model, since the former always implies the latter (but not vice versa). In the presence of a strong external magnetic field these transitions are smeared out and the different ferronematic phases become more similar to each other.

In chapter 3 we derive hydrodynamic equations for nematic ferrofluids (ferronematics) in the limit that the magnetic degree of freedom has relaxed to its equilibrium value. Hydrodynamics describes a system in the long wavelength limit and for long time scales. The hydrodynamic equations are derived by means of symmetry and thermodynamic arguments. The main advantage of the hydrodynamic method lies in its generality, which allows its application to very different systems. However, the occurrence of phenomenological parameters in the static and dynamic expansions are the prize one has to pay for this generality. Therefore coefficients turning up in the equations below have to be determined by microscopic models or by experiments.

We concentrate on novel dynamic effects linear in the magnetic field. We show that flow alignment, heat conduction, diffusion, thermodiffusion, viscosity and director reorientation are all modified by the presence of an external field. In particular, the new effects describe reversible (irreversible) couplings, where the conventional effects are irreversible (reversible). We discuss, how these effects can be measured. In principle, this description is applicable to conventional nematics, too, although huge magnetic fields are expected to be necessary for detecting the new effects in this case.

In chapter 4 we include the magnetization as an independent dynamic degree of freedom, thus deriving the complete set of macroscopic dynamic equations for ferrofluids in the nematic liquid crystal phase under an external magnetic field. To derive these equations, the hydrodynamic method has to be generalized.

This an example, where non-hydrodynamic, relaxing processes become so slow that their dynamics takes place on a macroscopic time scale as well. Then it is appropriate also to include non-hydrodynamic, but slowly relaxing variables in the dynamic description of such a system. However, there are no first principles to select those slowly relaxing variables and heuristic arguments have to be used instead. Such a phenomenological macroscopic description does not have the solid foundation of a truly hydrodynamic theory. On the other hand, by comparing the implications of this extended description with experiments, one can learn for which systems, and under what conditions, the inclusion of those non-hydrodynamic variables is required for a reasonable description.

Special emphasis is laid on possible static and dynamic cross-couplings between magnetization, director reorientations and flow. As examples we discuss the field dependence of the sound spectrum and the rheology of shear flow.

In chapter 5 we construct the macroscopic dynamic equations for a ferrogel using the hydrodynamic method described above. We include the deformations of a gel and the magnetization as independent dynamical variables. The magneto-mechanical cross-couplings between elasticity and the magnetic degree of freedom are introduced. In particular we discuss static elongation, shear and the modified sound spectrum in a homogeneous magnetic field by solving the appropriate generalized hydrodynamic equations.

Chapter 2

Landau description of ferrofluid to ferronematic phase transition*

2.1 Introduction

To study phase transitions in a ferronematic, the Landau mean field theory is used. The theory is based on a power series expansion of the free energy in terms of one or more oder parameters. It assumes, that the order parameter is small and uniform near the transition point so that only the lowest order terms allowed by symmetry are kept.

The starting point of our approach is to determine the order parameters. In order to obtain the isotropic-nematic phase transition, we make use of the nematic order parameter originally proposed by de Gennes [29], a symmetric, traceless tensor described by $Q_{ij} = \frac{1}{2}S(3n_in_j - \delta_{ij})$. The unit vector $\boldsymbol{n}$ describes the orientation of the nematic ordering. Since the nematic order does not discriminate between "up" and "down" along the preferred direction, $\boldsymbol{n}$ and $-\boldsymbol{n}$ are equivalent and $\boldsymbol{n}$ is called a director. Q_{ij} is the simplest tensorial quantity compatible with this up-down symmetry. The quantity S defines the strength of the nematic ordering (the modulus of the nematic order parameter) and is zero (one) for complete disorder (order). Thus in the isotropic phase $S = 0$ and in the nematic phase $S \neq 0$.

The magnetic order is described by the magnetization $\boldsymbol{M} = M\boldsymbol{m}$ whose modulus M is zero in a (super)paramagnetic and non-zero in a ferromagnetic state. The unit vector $\boldsymbol{m}$ denotes the orientation of the magnetic ordering. It is an axial vector, which is odd under time reversal symmetry (like a magnetic field).

We are now in the position to write down the Landau free energy ε for a ferronematic, which we study first for the case without, and second with a magnetic field.

2.2 Phase transitions without field

We first discuss phase transitions in the absence of an external field, using the nematic and the magnetization order parameters defined above. Keeping terms up to quartic order the total free energy density near the isotropic/nematic and para-/ferromagnetic transition can be written

*This chapter is based on ref. [28]

as:

$$\begin{aligned}\varepsilon &= \varepsilon_0 + \frac{A}{2}Q_{ij}Q_{ij} - \frac{B}{3}Q_{ij}Q_{jk}Q_{ki} + \frac{C_1}{4}(Q_{ij}Q_{ij})^2 + \frac{C_2}{4}Q_{ij}Q_{jk}Q_{kl}Q_{li} \\ &+ \frac{\alpha}{2}\boldsymbol{M}^2 + \frac{\beta}{4}\boldsymbol{M}^4 + \frac{\gamma}{2}M_iM_jQ_{ij} + \frac{\delta_1}{2}\boldsymbol{M}^2Q_{ij}Q_{ij} + \frac{\delta_2}{2}M_iM_kQ_{ij}Q_{kj} \end{aligned} \tag{2.1}$$

where ε_0 is the free energy density of the isotropic (superparamagnetic) ferrofluid phase. The change of sign of $A \equiv A_0(T - T^*_{NI})$ and $\alpha \equiv \alpha_0(T - T^*_{FP})$ at the critical temperatures T^*_{NI} and T^*_{FP} corresponds to a hypothetical second order isotropic to nematic, and to the para- to ferromagnetic transition, respectively, if the cross coupling terms ($\sim \gamma$ and $\sim \delta_{1,2}$) are absent. All other coefficients, as well as A_0 and α_0, are assumed to be constant near the transition point. For pressure - or (more likely) - concentration-driven phase transitions one could write $A \equiv A_c(c - c^*_{NI})$ and $\alpha \equiv \alpha_c(c - c^*_{FP})$ with a change in sign at some critical concentrations of ferroparticles. For simplicity we will stick to the temperature related notation in the following.

In addition to the bi-quadratic couplings between the nematic and magnetic order governed by the coupling coefficients $\delta_{1,2}$, there is also a cubic coupling ($\sim \gamma$), which is most important for these transitions. As will be discussed below, it is responsible for the fact that magnetic order induces the nematic order. As we shall see, negative (positive) values of $\delta_{1,2}$ favor (disfavor) ferromagnetic nematics over the (super)paramagnetic ferronematics.

We assume C_1, C_2, β and $\beta C_{1,2} - \delta^2_{1,2}$ to be positive to guarantee the stability of the isotropic phase at high temperatures and $B > 0$ to get $S > 0$ in the ferronematic phases, which is suitable for rod-like nematogens.

Here we consider phases in which the nematic and magnetic order are spatially invariant, $S = const.$ and $M = const.$, and the ordering directions $\boldsymbol{n}$ and $\boldsymbol{m}$ make an angle ψ, i.e. $\boldsymbol{n} \cdot \boldsymbol{m} = \cos\psi$. In that case eq.(2.1) reads

$$\begin{aligned}\varepsilon - \varepsilon_0 &= \frac{3}{4}AS^2 - \frac{1}{4}BS^3 + \frac{9}{16}CS^4 + \frac{1}{2}\alpha M^2 + \frac{1}{4}\beta M^4 + \frac{3}{4}\delta_1 M^2 S^2 \\ &+ \frac{1}{8}\delta_2 M^2 S^2(3\cos^2\psi + 1) + \frac{1}{4}\gamma M^2 S\,(3\cos^2\psi - 1)\end{aligned} \tag{2.2}$$

where $C \equiv C_1 + C_2/2$. The presence of the cubic terms ($\sim B$ and $\sim \gamma$) describes the first order character of the isotropic ferrofluid to ferronematic transitions. Eq.(2.2) has a structure quite similar to that of a Landau free energy for the isotropic to smectic A phase transition in conventional thermotropic liquid crystals [30].

Minimization of eq.(2.2) with respect to S, M and ψ yields the following three phases:

$$\text{Isotropic Ferrofluid (I):} \quad S = 0, \quad M = 0, \quad \psi = \text{undefined} \tag{2.3}$$

$$\begin{aligned}\text{Paramagnetic Nematic (N):} \quad & S_N = \frac{1}{6C}\left[B + (B^2 - 24AC)^{1/2}\right] > 0, \\ & M = 0, \quad \psi = \text{undefined}\end{aligned} \tag{2.4}$$

$$\begin{aligned}\text{Ferromagnetic Nematic (F):} \quad & S_F > 0, \quad M^2 = -\frac{1}{\beta}\Big(\alpha + \tilde{\gamma}S_F + \tilde{\delta}S_F^2\Big), \\ & \psi = 0 \text{ or } \pi/2\end{aligned} \tag{2.5}$$

where S_F is defined by

$$-\frac{2}{3}\frac{\alpha\tilde{\gamma}}{\beta} + 2A^*S_F - B^*S_F^2 + 3C^*S_F^3 = 0 \tag{2.6}$$

with the abbreviations $A^* = A-(2/3\beta)\tilde{\delta}\alpha-(1/3\beta)\tilde{\gamma}^2$, $B^* = B+(2/\beta)\tilde{\delta}\tilde{\gamma}$ and $C^* = C-(4/9\beta)\tilde{\delta}^2$. The new coefficients $\tilde{\delta}$ and $\tilde{\gamma}$ depend on the angle ψ and are

$$\tilde{\delta} = \begin{cases} \frac{3}{2}\delta_1 + \delta_2 \\ \frac{3}{2}\delta_1 + \frac{1}{4}\delta_2 \end{cases} \qquad \tilde{\gamma} = \begin{cases} \gamma & \text{for} \quad \psi = 0 \\ -\frac{1}{2}\gamma & \text{for} \quad \psi = \pi/2 \end{cases} \tag{2.7}$$

There is no extremum of (2.1) with $S = 0$ and $M \neq 0$, i.e. no ferromagnetic phase without nematic ordering. This can easily be seen directly from the coupling term $\sim \gamma$ in (2.1), where a finite M^2 acts as an external "field" on the nematic order, thus inducing a non-zero S.

Necessary conditions for the different phases to be stable are

$$\frac{\partial^2\varepsilon}{\partial S^2} > 0, \qquad \frac{\partial^2\varepsilon}{\partial M^2} > 0, \qquad \frac{\partial^2\varepsilon}{\partial\psi^2} > 0, \qquad \frac{\partial^2\varepsilon}{\partial S^2}\frac{\partial^2\varepsilon}{\partial M^2} - \left(\frac{\partial^2\varepsilon}{\partial S\,\partial M}\right)^2 > 0 \tag{2.8}$$

The derivatives in (2.8) have to be taken at the values (2.3-2.5) for the appropriate phases. For the isotropic ferrofluid phase the stability conditions are simply $\alpha > 0$ and $A > 0$. The paramagnetic nematic phase is stable, if $\alpha + \tilde{\gamma}S + \tilde{\delta}S^2 > 0$ and $24AC < B^2$.

The possible orientation between nematic and magnetic ordering in the ferromagnetic phase, either parallel ($\psi = 0$) or orthogonal ($\psi = \pi/2$), is fixed by the third stability condition in (2.8), where the former (latter) orientation is obtained for $\delta_2 S_F + 2\gamma < 0$ (> 0). Thus, a negative (positive) γ favors parallel (orthogonal) orientation. In the parallel case the phase has uniaxial $D_{\infty h}$ symmetry (as conventional nematics), while in the orthogonal case the phase is biaxial with orthorhombic D_{2h} symmetry. For ψ a value different from zero or ninety degrees could only be obtained by taking into account terms higher than forth order in the Landau expansion, a procedure, for which there is no a priori reason. The other stability conditions for the ferromagnetic case read

$$A - BS_F + \frac{9}{2}CS_F^2 + \frac{2}{3}\tilde{\delta}M^2 > 0 \tag{2.9}$$

$$\alpha + \tilde{\gamma}S_F + \tilde{\delta}S_F^2 < 0 \tag{2.10}$$

$$A^* - B^*S_F + \frac{9}{2}C^*S_F^2 > 0 \tag{2.11}$$

ensuring S_F and M^2 to be positive quantities. Obviously, a negative $\tilde{\delta}$ enhances the stability of the ferromagnetic phase. These stability conditions determine the existence ranges (in terms of temperature) of the different phases rather implicitly. The existence ranges of all three phases generally overlap. That phase with the lowest free energy is the stable one. A (first order) transition takes place, when 2 free energies are identical. The isotropic ferrofluid to paramagnetic nematic transition, thus, takes place, when the right hand side of (2.2) is zero taking for M and S the values (2.4). This happens for $A = B^2/27C$ leading to a transition temperature $T_{NI} = T_{NI}^* + B^2/27CA_0$ somewhat larger than the critical transition temperature of the hypothetical second order transition.

The transition from the paramagnetic nematic phase (with finite S_N) to the ferromagnetic one is then described by (2.2), which takes the form

$$\varepsilon - \varepsilon_N = \frac{1}{2}\tilde{\alpha}M^2 + \frac{1}{4}\beta M^4 \tag{2.12}$$

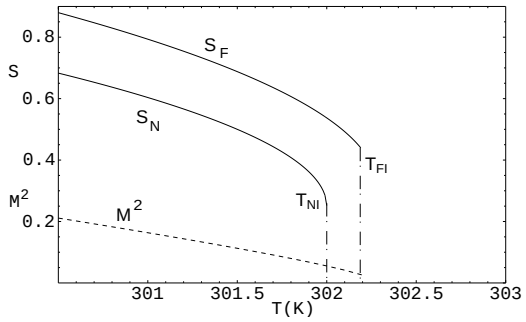

Figure 2.1: S and M^2 versus temperature. The upper (lower) solid line represents the orientational order parameter S_F (S_N), while the dashed line represents the (dimensionless) magnetic order parameter M^2 in the ferromagnetic phase. The values of the parameters in eq.(2.2) were taken to be $\alpha_0 = .1K^{-1}$, $A_0 = .1K^{-1}$, $T^*_{NI} = 301.7K$, $T^*_{FP} = 302K$, $B = .8$, $C = .53$, $\beta = 8$, $\tilde{\delta} = -.89$ (for the FI transition), $\tilde{\delta} = .16$ (for the NI transition), and $\tilde{\gamma} = -.05$ using a dimensionless free energy density f.

where ε_N is the free energy of the paramagnetic nematic and $\tilde{\alpha} = \alpha + \tilde{\gamma} S_N + \tilde{\delta} S_N^2$. Obviously that transition is of second order and takes place at the temperature $T = T^*_{FP} - (1/\alpha_0)(\tilde{\gamma} S_N + \tilde{\delta} S_N^2)$, which is shifted from the critical para- to ferromagnetic transition temperature due to the finite nematic order. This shift can be negative as well as positive, i.e. the existing nematic order can favor or disfavor an additional ferromagnetic ordering. Again, a negative $\tilde{\delta}$ favors the ferromagnetic ordering.

Of course, there is the competing possibility of a direct transition from the isotropic ferrofluid to the ferromagnetic nematic phase. Substituting the solution (2.5) for the magnetic order parameter $M \neq 0$ and for ψ into the free energy (2.2) we get the free energy density for the ferromagnetic phase as a function of S_F alone, which can be written as

$$\varepsilon - \varepsilon_0 = -\frac{\alpha^2}{4\beta} - \frac{\alpha\tilde{\gamma}}{2\beta} S_F + \frac{3}{4} A^* S_F^2 - \frac{1}{4} B^* S_F^3 + \frac{9}{16} C^* S_F^4 \tag{2.13}$$

where the starred coefficients are defined after (2.6). Of the 3 possible extrema ($\frac{\partial \varepsilon}{\partial S} = 0$ leading to a real solution for S_F) only those are relevant that exist within the stability range of the ferromagnetic phase. Although the solutions are involved, one important qualitative feature can be extracted immediately. It is obvious that a continuous IF transition ($S_F = 0 = M$ at the transition temperature) is not possible, except for the very special case $B = 0 = \gamma$ (involving $B^* = 0 = \tilde{\gamma}$) and $T^*_{NI} = T^*_{FP}$. In the general case there is a jump in S_F and M at some temperature T_{FI}. At that temperature the right hand side of (2.13) is zero for S_F given by eq.(2.6). Of course, T_{FI} has to be larger than T_{NI} for the direct transition to happen. Such a case is shown in Fig.2.1 by choosing an appropriate set of parameters and numerically solving (2.6). Fig.2.1 shows that both order parameters, S_F and M jump simultaneously at the FI transition point. We also see that orientational order in the ferromagnetic phase is much higher than in the (superparamagnetic) nematic phase.

It is interesting to note that this phase transition is isomorphic to the direct isotropic to smectic A transition for ordinary liquid crystals, where the role of the magnetic order is played by the smectic order [30].

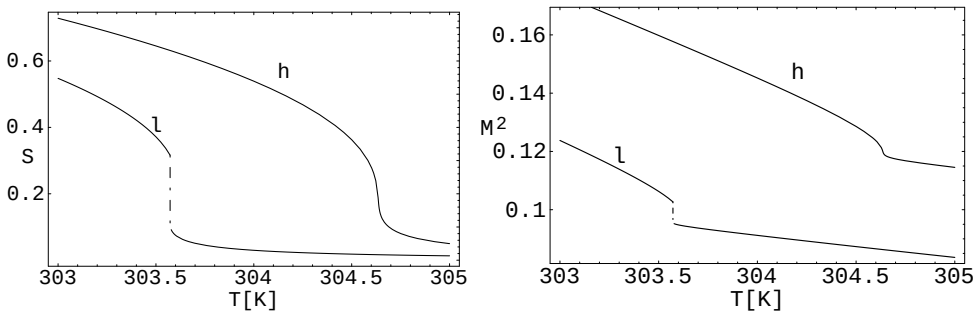

Figure 2.2: $S(T)$ and $M^2(T)$ according to eqs. (2.15,2.16) for two different values of the external magnetic field with $\boldsymbol{n}$ and $\boldsymbol{M}$ parallel. The transition to the ferromagnetic state ($\tilde{\delta} = -.89$) is discontinuous for (l) lower fields ($H = .28$) and becomes smooth for (h) higher fields ($H = .41$). We have chosen $\chi_S = .05$ and $\delta_3 + (2/3)\delta_4 = -.89$; all other parameters are as in Fig.2.1.

2.3 Phase transitions in an external field

An external field induces a finite magnetization in the ferrofluid by orienting the magnetic particles. In addition it also orients the mesogens due to the diamagnetic anisotropy effect. Thus, any phase has a finite S and a finite M due to the external field. This is also obvious from the Landau free energy including the external field $\boldsymbol{H}$

$$\varepsilon_H = \varepsilon - \boldsymbol{M}\cdot\boldsymbol{H} - \frac{\chi_S}{2}H_iH_jQ_{ij} + \frac{\delta_3}{2}\boldsymbol{H}^2Q_{ij}Q_{ij} + \frac{\delta_4}{2}H_iH_kQ_{ij}Q_{kj} \tag{2.14}$$

with ε the field-free energy (2.1). The angle between the magnetization and the field is dominated by the ferromagnetic coupling $-\boldsymbol{M}\cdot\boldsymbol{H}$ with $\boldsymbol{M}$ parallel to $\boldsymbol{H}$ being the ground state. Thus, the angle ψ between $\boldsymbol{M}$ and $\boldsymbol{n}$ is also the angle between $\boldsymbol{H}$ and $\boldsymbol{n}$. As we show later there are three possibilities for the orientation of $\boldsymbol{n}$ and $\boldsymbol{M}$ with respect to the magnetic field.

The diamagnetic coupling ($\sim \chi_S$) and the higher coupling term ($\sim \delta_4$) have the same ψ-dependence as the γ- and δ_2 terms in (2.2) leading again to the free energy extrema at $\psi = 0$ or $\pi/2$. The former (latter) is the stable minimum for $[(\delta_2 S + 2\gamma)M^2 + (\delta_4 S - 2\chi_S)H^2]S < 0$ (> 0). The latter case seems to be frequent in discotic lyotropic [19] and rod-like thermotropic nematic systems [20].

Minimizing then (2.14) with respect to S and M leads to the coupled equations for $S(H)$ and $M(H)$

$$0 = -\tilde{\chi}_S H^2 + 3\tilde{A}S - \frac{3}{2}BS^2 + \frac{9}{2}CS^3 + 2\tilde{\delta}M^2S + \tilde{\gamma}M^2 \tag{2.15}$$

$$0 = -H + \alpha M + \beta M^3 + \tilde{\delta}MS^2 + \tilde{\gamma}MS \tag{2.16}$$

with $\tilde{A} = A + H^2(\delta_3 + (2/3)\delta_4)$ and $\tilde{\chi}_S = \chi_S$ for $\psi = 0$, and $\tilde{A} = A + H^2(\delta_3 + (1/6)\delta_4)$ and $\tilde{\chi}_S = (-1/2)\chi_S$ for $\psi = \pi/2$. Also there is a third possibility for the orientation of $\boldsymbol{n}$ and $\boldsymbol{M}$ with respect to the external field $\boldsymbol{H}$: None is parallel to another one, but all three lie in a common plane separated by the angles ψ and ϕ (between $\boldsymbol{M}$ and $\boldsymbol{H}$). These angles are determined by the relations $HM\sin\phi = (3/8)SM^2(\delta_2 S + 2\gamma)\sin 2\psi = (3/8)SH^2(\delta_4 S - 2\chi_S)\sin 2(\phi - \psi)$. Again, $S(H)$ and $M(H)$ follow from equations of the form (2.15,2.16), where the coefficients,

however, are very complicated. Since such a case has not been found in experiment, we will not discuss it further.

Obviously there is no solution of (2.15, 2.16) with $S = 0$ and/or $M = 0$ for finite magnetic field. Instead, even the high temperature phase shows a small but finite nematic as well as magnetic order both induced by the external field. For the transition to the ferromagnetic nematic phase, where M acquires a spontaneous contribution in addition to the field-induced one, both jumps (in M and S) are reduced (and shifted to higher temperatures) and eventually, above some strong external fields, are replaced by smooth passages from low to high values (Fig.2.2). This field dependence of S resembles the isotropic-nematic transition in the presence of an external *electrical* field [31]. In conventional nematics this behavior under an external magnetic field has never been observed, since the strong fields necessary are outside the experimental reach, while in ferronematics the expectation is that the necessary magnetic fields are much smaller and thus this effect is detectable.

The transition to the superparamagnetic nematic state (for positive coupling coefficients $\delta_{1,2,3,4}$) is again characterized by a jump from small S to a larger value of S, where the jump decreases with increasing field and eventually vanishes leading to a smooth passage from a low S to a high S state. For large coupling coefficients the transition temperature is shifted to lower values and at the transition the field-induced value of M is reduced due to the coupling to S, either discontinuously (low fields) or smoothly (large fields). For smaller coupling coefficients the transition temperature is almost field-independent and M is hardly affected by the change of S.

2.4 Summary

Here we discussed possible phase transitions as a function of temperature (or pressure or ferrofluid particle concentration) between an isotropic ferrofluid phase, the superparamagnetic and the ferromagnetic nematic phase. Using a Landau-de Gennes expansion of a nematic and a magnetic order parameter up to fourth order, we found that depending on the signs and magnitude of the cross-couplings between nematic and magnetic order there is the possibility to have either a direct FI transition or a two-step NI and FN transition. Similarities to the isotropic-nematic-smectic A transitions in ordinary liquid crystals are discussed. In the ferromagnetic phase the magnetic and the nematic orientations are either parallel or orthogonal. In an external magnetic field in addition there is a third possibility: the magnetization, the director and the magnetic field orientations are different, but lie in a common plane. In the present model there is no possibility to have a ferromagnetic phase that lacks nematic ordering. In the last section we studied the phase transitions in an external magnetic field. We showed how the jumps of the order parameters are reduced by the presence of an external field and eventually are completely smeared out, if the field is strong enough. Then, the superparamagnetic and the ferromagnetic nematic phases are identical in their symmetry properties and differ only quantitatively in the value of M. Thus, a clear distinction is best made at vanishing external field.

Chapter 3

Hydrodynamics of ferronematics[†]

3.1 Introduction

Owing to the admixture of magnetic particles to a nematic both, the nematic and the magnetic degree of freedom generally have to be taken into account. However, we will restrict ourselves here to situations where the magnetization has relaxed to its equilibrium value parallel to the applied magnetic field (the case, when the magnetization is an independent variable is discussed in the chapter 4). It is then a function of all state variables (and the external field), but has no independent dynamics, i.e. magnetic relaxation effects are disregarded here. This is a good approximation for times shorter than typical magnetic relaxation times (10^{-4} to $10^{-6}s$). Since the nematic director dynamics is much slower, it is appropriate to keep explicitly the latter (this has nothing to do with the "rigid anchoring" approximation mentioned above, since $\boldsymbol{n}$ can have any orientation relative to $\boldsymbol{M}$). This description is, thus, in principle also valid for ordinary nematics, where no magnetic degree of freedom is present. However, the new effects described here probably require huge magnetic fields to be observable in ordinary nematics, while in ferronematics their detection should be much easier. In ordinary nematics the diamagnetic interaction energy adding up to the director's molecular field is usually considered to be the only relevant magnetic contribution. However, in ferronematics other effects disregarded so far mostly (except in [33]) might become significant. In the following we will concentrate on those effects, which are *linear* in the magnetic field strength H. As this quantity is of negative parity under time reversal such effects can arise in the dynamics only and a variety of new Onsager couplings will appear. These new couplings change the character of the contributions in the field free case from reactive to dissipative or vice versa. The implications of these new couplings will be illustrated by means of a series of different examples.

3.2 Nematodynamics without magnetic field

Nematic liquid crystals are characterized by an extended set of hydrodynamic variables that comprise those of a simple liquid (density ρ, momentum density $\rho\boldsymbol{v}$ related to the velocity $\boldsymbol{v}$, and entropy density σ, or equivalently energy density ε) and in addition the director $\boldsymbol{n}$, the symmetry variable denoting orientational changes ($\boldsymbol{n}^2 = 1$) of the preferred direction and, in

[†]This chapter is based on ref. [32]

the case of mixtures, the concentration c. In our case the latter is the concentration of the ferromagnetic particles. The hydrodynamic equations are [29,34,35]

$$\frac{\partial}{\partial t}\rho + div\,\rho\boldsymbol{v} = 0 \tag{3.1}$$

$$\frac{\partial}{\partial t}g_i + \nabla_j\Big(v_j g_i + \delta_{ij}p + \Phi_{kj}\nabla_i n_k + \sigma_{ij}\Big) = 0 \tag{3.2}$$

$$\Big(\frac{\partial}{\partial t} + v_j\nabla_j\Big)n_i + (\boldsymbol{n}\times\boldsymbol{\omega})_i + Y_i = 0 \tag{3.3}$$

$$\rho\Big(\frac{\partial}{\partial t} + v_j\nabla_j\Big)c + div\,\boldsymbol{j}^c = 0 \tag{3.4}$$

$$\frac{\partial}{\partial t}\sigma + div\,\sigma\boldsymbol{v} + div\boldsymbol{j}^\sigma = \frac{R}{T} \tag{3.5}$$

Generally the densities of the currents for heat $\boldsymbol{j}^\sigma$, concentration $\boldsymbol{j}^c$, and momentum, the stress tensor σ_{ij} and the quasi-current Y_i are the sum of two parts, a reversible and an irreversible one, where the former (latter) has the same (opposite) time reversal symmetry as the rest of the equation and leads to zero (positive) entropy production, i.e. it is reactive (dissipative). Within irreversible thermodynamics the dissipative parts can be derived from the dissipation function R (the source term in (3.5)) as a potential, while the reversible ones do not follow from any potential [36]. The currents read

$$\sigma_{ij} = -\frac{1}{2}\lambda_{kji}h_k - \nu^D_{ijkl}\nabla_l v_k \tag{3.6}$$

$$Y_i = -\frac{1}{2}\lambda_{ijk}\nabla_j v_k + \frac{1}{\gamma_0}\delta^\perp_{ij}h^n_j \tag{3.7}$$

$$j^\sigma_i = -\kappa_{ij}\nabla_j T - D^T_{ij}\nabla_j\mu_c \tag{3.8}$$

$$j^c_i = -D_{ij}\nabla_j\mu_c - D^T_{ij}\nabla_j T \tag{3.9}$$

with the transverse Kronecker symbol $\delta^\perp_{ij} \equiv \delta_{ij} - n_i n_j$. The conjugate quantities temperature $T = T(\rho,\sigma,c)$, pressure $p = p(\rho,\sigma,c)$, relative chemical potential $\mu_c(\rho,\sigma,c)$, and the 'molecular fields' $h^n_i(\rho,\sigma,c)$ and $\Phi_{ij}(\rho,\sigma,c)$ follow from the free energy density ε (see below (3.13)). This part of the equations, which constitutes the statics of the system, is derived completely independently from the dynamics, eqs.(3.6-3.9).

The heat conduction tensor κ_{ij}, the diffusion tensor D_{ij} as well as thermodiffusion tensor D^T_{ij} (related to the Soret/Dufour effects) are symmetric and have the following form containing together six coefficients (thermal conductivity, diffusivity and Soret/Dufour),

$$\kappa_{ij} = \kappa_\perp\delta^\perp_{ij} + \kappa_\parallel\, n_i n_j \tag{3.10}$$

The tensor λ_{ijk}, describing flow alignment in (3.7) and back flow in (3.6) contains one phenomenological parameter

$$\lambda_{ijk} = (\lambda-1)\delta^\perp_{ij}n_k + (\lambda+1)\delta^\perp_{ik}n_j \tag{3.11}$$

which is reversible, since h^n_i, Y_i and σ_{ij} all do not change sign under time reversal.

The fourth rank viscosity tensor contains five viscosities

$$\begin{aligned}\nu^D_{ijkl} &= \nu_2(\delta_{jl}\delta_{ik}+\delta_{il}\delta_{jk})\\ &\quad +2(\nu_1+\nu_2-2\nu_3)n_in_jn_kn_l\\ &\quad +(\nu_3-\nu_2)(n_jn_l\delta_{ik}+n_jn_k\delta_{il}+n_in_k\delta_{jl}+n_in_l\delta_{jk})\\ &\quad +(\nu_4-\nu_2)\delta_{ij}\delta_{kl}\\ &\quad +(\nu_5-\nu_4+\nu_2)(\delta_{ij}n_kn_l+\delta_{kl}n_in_j)\end{aligned} \tag{3.12}$$

3.3 Static relations

The statics of a macroscopic system is governed by its free energy. For nematics the free energy density in harmonic approximation reads [29, 34, 35]

$$\begin{aligned}\varepsilon &= \frac{T}{2C_V}(\delta\sigma)^2+\frac{1}{2\rho^2\kappa_s}(\delta\rho)^2+\frac{\gamma}{2}(\delta c)^2+\frac{1}{\rho\alpha_s}(\delta\sigma)(\delta\rho)\\ &\quad +\beta_\sigma(\delta c)(\delta\sigma)+\beta_\rho(\delta c)(\delta\rho)+\frac{1}{2}K_{ijkl}(\nabla_jn_i)(\nabla_ln_k)\end{aligned} \tag{3.13}$$

where the Frank tensor

$$K_{ijkl}=K_1\delta^\perp_{ij}\delta^\perp_{kl}+K_2n_p\epsilon_{pij}n_q\epsilon_{qkl}+K_3n_jn_l\delta^\perp_{ik} \tag{3.14}$$

describes the energy cost for distorting the homogeneous alignment of the director. The conventional static susceptibilities contained in (3.13) are the specific heat (at constant density) C_V, the isentropic compressibility κ_s, the adiabatic volume expansion coefficient α_s and the appropriate susceptibilities γ, β_σ and β_ρ related to the concentration instead of the total mass density.

Due to the Gibbs relation (the local manifestation of the first and second law of thermodynamics)

$$d\varepsilon=\mu\,d\rho+T\,d\sigma+\mu_c\,dc+v_i\,dg_i+\Phi_{ij}\,d\nabla_jn_i+h^{n\prime}_i\,dn_i \tag{3.15}$$

the conjugate quantities follow from the free energy density by partial differentiation

$$\delta T \equiv \frac{\partial f}{\partial\sigma}=\frac{T}{C_V}\delta\sigma+\frac{1}{\rho\alpha_s}\delta\rho+\beta_\sigma\delta c \tag{3.16}$$

$$\delta\mu \equiv \frac{\partial f}{\partial\rho}=\frac{1}{\rho^2\kappa_s}\delta\rho+\frac{1}{\rho\alpha_s}\delta\sigma+\beta_\rho\delta c \tag{3.17}$$

$$\delta\mu_c \equiv \frac{\partial f}{\partial c}=\gamma\,\delta c+\beta_\sigma\delta\sigma+\beta_\rho\delta\rho \tag{3.18}$$

$$\Phi_{ij} \equiv \frac{\partial f}{\partial\nabla_jn_i}=K_{ijkl}\nabla_ln_k \tag{3.19}$$

$$h^{n\prime}_i \equiv \frac{\partial f}{\partial n_i}=\delta^\perp_{iq}\frac{\partial K_{pjkl}}{2\,\partial n_q}(\nabla_ln_k)(\nabla_jn_p) \tag{3.20}$$

The response to static director deformations is given by

$$h_i^n \equiv \frac{\delta}{\delta n_i} \int f dV = h_i^{n\prime} - \nabla_j \Phi_{ij} \tag{3.21}$$

The pressure is related to the other conjugate quantities by the Gibbs-Duhem relation [34]

$$\delta p = \rho \delta \mu + \sigma \delta T - \mu_c \delta c - h_j \delta n_j \tag{3.22}$$

neglecting contributions quadratic in the velocity.

3.4 Dynamics in a magnetic field

3.4.1 Linear vs. quadratic field effects

Let's consider nematics in a magnetic field. The effect of an external magnetic field H on the statics is rather simple. Since all static equations have to be invariant under time reversal symmetry, and H changes sign under this symmetry, only quadratic contributions to the free energy are allowed in lowest order

$$\varepsilon^{(M)} = -\frac{1}{2}\chi_a (\boldsymbol{H} \cdot \boldsymbol{n})^2 \tag{3.23}$$

which is the diamagnetic anisotropy energy [29] giving rise to the magnetic molecular field (3.24). Depending on the sign of χ_a the static orientation of $\boldsymbol{n}$ is either parallel or perpendicular to $\boldsymbol{H}$. An external field breaks the rotational symmetry externally and n_i relaxes according to the diamagnetic anisotropy to its equilibrium orientation. The appropriate molecular field h_i^n reads

$$h_i^{(M)} = -\chi_a H_i (\boldsymbol{n} \cdot \boldsymbol{H}) \tag{3.24}$$

Usually this is the only effect of an external magnetic field that is taken into account when dealing with ordinary nematic liquid crystals. All other effects (a few of them are discussed in [33]) are assumed to be small and are neglected. In ferronematics the response to an external magnetic field is rather enhanced and such hitherto disregarded effects can become important. There is the (rather trivial) effect that all material coefficients (transport parameters and susceptibilities) can depend on H^2. In addition, if $\boldsymbol{n}$ is perpendicular to $\boldsymbol{H}$ in equilibrium, the system is biaxial and the uniaxial tensors in eqs. (3.10, 3.11, 3.12) are of the well-known biaxial form. Furthermore, there are the magnetic forces, which are described by the Maxwell stress $\sigma_{ij}^{(M)} = -\mu_{eq}(H) H_i H_j$ with the equilibrium magnetic susceptibility $\mu_{eq}(H)$ [1] and by a redefinition of the pressure $p \to p - (1/2)H^2$. However, all these effects (including (3.24)) are quadratic in the external field strength and represent additions to effects already present. In the following we will discuss additional effects that are linear in the field and represent new effects thus bearing a good chance of being observable in ferronematics.

Since a magnetic field changes sign under time reversal, linear effects are possible in the dynamics only, since in the statics all relations are time-reversal symmetric, that is invariant under time reversal. In the dynamics the currents come in two classes, either reversible or irreversible, meaning time-reversal symmetric and antisymmetric, respectively. The introduction of a linear field then toggles between these two possibilities.

3.4.2 Flow alignment

As a first example we will consider flow alignment in the presence of a magnetic field. The flow alignment tensor (3.11) can have additions linear in the field

$$\begin{aligned}\lambda^D_{ijk}(H) \;=\; & \lambda^D_1\left(\delta^\perp_{iq}\epsilon_{pjq}H_p n_k + \delta^\perp_{iq}\epsilon_{pkq}H_p n_j\right)\\ & +\lambda^D_2\left(\delta^\perp_{ik}H_p\epsilon_{pjq}n_q + \delta^\perp_{ij}H_p\epsilon_{pkq}n_q\right)\\ & +\lambda^D_3\left(H_j\epsilon_{ipk}n_p + H_k\epsilon_{ipj}n_p\right)\\ & +\lambda^D_4\left(H_q n_q n_j\epsilon_{ipk}n_p + H_q n_q n_k\epsilon_{ipj}n_p\right)\\ & +\lambda^D_5 H_p\epsilon_{piq}n_q n_j n_k + \lambda^D_6 H_p\epsilon_{piq}n_q\delta^\perp_{jk}\end{aligned} \tag{3.25}$$

Note that these contributions are all dissipative while (3.11) represents only reversible ones. Adding up in eq.(3.7) both contributions into $\lambda^{(Y)}_{ijk} \equiv \lambda_{ijk} + \lambda^D_{ijk}(H)$ then the cross coupling term in (3.6) reads $\lambda^{(\sigma)}_{kji} \equiv \lambda_{kji} + \lambda^D_{kji}(-H) = \lambda_{kji} - \lambda^D_{kji}(H)$ due to Onsager's relation[1] guaranteeing a positive (zero) entropy production due to the field-dependent (-independent) parts.

In the stationary case all currents and quasi currents are zero (disregarding the thermal degree of freedom here)

$$\nabla_i(p\delta_{ij} + \Phi_{lj}\nabla_i n_l + \sigma_{ij}) = 0, \quad \text{and} \quad (\boldsymbol{n}\times\boldsymbol{\omega})_i + Y_i = 0. \tag{3.26}$$

The first condition is identically satisfied for constant shear flow and constant field. The second one

$$-\frac{1}{2}\lambda^{(Y)}_{ijk}\nabla_j v_k + \frac{1}{\gamma_0}\delta^\perp_{ik}h^{(M)}_k = 0 \tag{3.27}$$

reads explicitly

$$\begin{aligned} & n_k(\lambda-1)\nabla_i v_k + n_j\nabla_j v_i(\lambda+1) - 2\lambda n_i n_j n_k\nabla_j v_k \\ & \quad +\lambda^D_{ijk}(H)\nabla_j v_k + \chi'_a H_i n_j H_j - \chi'_a n_i n_k H_k n_j H_j \;=\; 0,\end{aligned} \tag{3.28}$$

where $\chi'_a = 2\chi_a/\gamma_0$.

We will solve eq.(3.28) for a particular case, where the new linear field terms (3.25) become manifest: The external field lies in the shear plane

$$\begin{aligned} n_x &= \sin\theta\\ n_y &= \cos\theta\sin\varphi\\ n_z &= \cos\theta\cos\varphi\\ H_y &= H\sin\psi\\ H_z &= H\cos\psi\end{aligned} \tag{3.29}$$

with the shear flow $\nabla_z v_y = S$ and with ψ the angle of the magnetic field with the shear gradient.

[1] With the currents $C_\alpha \equiv \{Y_i\,,\,\sigma_{jk}\}$ the forces are $F_\beta \equiv \{h^n_i\,,\,-\nabla_j v_k\}$, since the entropy production $R \sim -h^n_i Y_i - v_k\nabla_j\sigma_{kj} \sim -h^n_i Y_i + \sigma_{kj}\nabla_j v_k$. Then, Onsager's relation $D_{\alpha\beta}(H) = \epsilon_\alpha\epsilon_\beta D_{\beta\alpha}(-H)$, with $C_\alpha = D_{\alpha\beta}F_\beta$, leads to the symmetries stated above for the λ-tensor, since $\epsilon_\alpha\epsilon_\beta = -1$ for cross terms connecting variables of different time reversal symmetry.

Without the new terms it is known that the director also lies in the shear plane (i.e. $\theta = 0$) making an angle φ with the direction of the shear gradient, where φ is given by

$$2S\left(\lambda\cos 2\varphi + 1\right) = \chi_a' H^2 \sin\left(2\left(\varphi - \psi\right)\right) \tag{3.30}$$

The new terms (except λ_2^D) force the director out of the shear plane. Taking first λ_1^D as a representative for the other terms (in order to simplify the formulas) we get the unchanged condition (3.30) for the in-plane orientation φ of the director. There is, however, now an out-of-plane component of the director given by the non-zero angle θ

$$\tan\theta = \frac{-\lambda_1^D SH \sin\varphi\cos(\varphi+\psi)}{(\lambda+1)\,S\cos\varphi + \chi_a' H^2 \sin\psi\cos(\psi-\varphi)} \tag{3.31}$$

This kinetic expulsion out of the shear plane due to the combined action of shear flow and (in-plane) field occurs, even if the (static) diamagnetic anisotropy would favor a director parallel to the field ($\chi_a > 0$), i.e. to be in-plane. Other contributions in (3.25) will change also the simple expression (3.30) for the in-plane components of $\boldsymbol{n}$. E.g. the two last contributions in (3.25) lead to an out-of-plane orientational angle

$$\tan\theta = \frac{\beta\sin^2\varphi}{2(\lambda\sin\varphi + \alpha\cos\varphi)} \tag{3.32}$$

with $2\alpha = \chi_a' H^2/S$ and $\beta = (\lambda_5^D - \lambda_6^D)H$. Here the in-plane-angle φ is not given by (3.30) but follows from

$$\frac{\beta^2\sin^3\varphi}{4(\lambda\sin\varphi+\alpha\cos\varphi)^2} = \frac{1+\lambda\cos 2\varphi - \alpha\sin 2\varphi}{(\lambda-1)\sin\varphi + 2\alpha\cos\varphi} \tag{3.33}$$

In (3.32) and (3.33) we have simplified the formulas by assuming $\psi = 0$, i.e. the magnetic field parallel to the shear gradient. For λ_3^D and λ_4^D the appropriate formulas are even more bulky and will not be shown here.

3.4.3 Heat conduction, diffusion and thermodiffusion

As a second example we consider the heat conduction tensor κ_{ij}. There are additions linear in the field of the form

$$\kappa_{ij}^R(H) \;=\; \kappa_1^R\epsilon_{ijk}H_k + \kappa_2^R\epsilon_{ijk}n_k n_p H_p + \kappa_3^R\left(\epsilon_{ipq}H_p n_q n_j - \epsilon_{jpq}H_p n_q n_i\right) \tag{3.34}$$

These terms are reversible due to their time reversal behavior, while those of (3.10) are irreversible. The former are antisymmetric $\kappa_{ij}^R(H) = \kappa_{ji}^R(-H) = -\kappa_{ji}^R(H)$ according to the Onsager's relation thus leading to zero entropy production.

The field-free heat conduction tensor (3.10) leads to a heat current $\boldsymbol{j}^\sigma = (\kappa_\parallel - \kappa_\perp)\,\boldsymbol{n}\,(\boldsymbol{n}\cdot\boldsymbol{\nabla}T)$ $+\kappa_\perp\boldsymbol{\nabla}T$ that lies in the plane of the director and the temperature gradient. The field-dependent terms lead to (reversible) contributions to the heat current that can be perpendicular to both, temperature gradient and field, or to temperature gradient and director, or to field and director.

For example, if the field H is along the x- and temperature gradient G along the y-direction, there is a reversible component of the heat current

$$j_z^\sigma = \begin{cases} (\kappa_1^R + \kappa_2^R)HG \\ (\kappa_1^R - \kappa_3^R)HG \end{cases} \qquad \text{for} \quad \boldsymbol{n} \parallel \begin{cases} \boldsymbol{H} \\ \boldsymbol{\nabla} T \end{cases} \tag{3.35}$$

that is orthogonal to the $\boldsymbol{n}/\boldsymbol{\nabla} T$ plane and perpendicular to the field. This effect is quite analogous to the Hall effect related to electric currents. There, similarly the diagonal elements (the analogues to (3.10)) are dissipative, while the antisymmetric parts (the analogues to (3.34)) are non-dissipative [37]. Instead of a voltage transverse to the dissipative electric current, eq.(3.35) leads to a temperature difference transverse to the dissipative heat current. This effect (especially the part related to κ_1^R) is in principle present in any fluid (and called Righi-Leduc effect [33]) and not restricted to ferronematics, but in the latter system chances are much better that it is observable.

Quite analogously to (3.34) one can introduce 3 new reversible diffusivities $D_{1,2,3}^R$ and the discussion between (3.34) and (3.35) can be taken over replacing ($\boldsymbol{j}^\sigma$, T) by ($\boldsymbol{j}^c$, μ_c). Rather similar is also the case of thermal diffusion. There are three reversible thermal diffusivities $D_{1,2,3}^{T,R}$ of the form (3.34). Since they are antisymmetric w.r.t. interchange of indices, and linear in the field, they automatically fulfill Onsager's relation $D_{ij}^{T,R}(H) = D_{ji}^{T,R}(-H)$. Under an external magnetic field (of strength H) orthogonal to a temperature gradient (of magnitude G) these new contributions give rise to a concentration current (orthogonal to both) given by the r.h.s. of (3.35), if the κ^R's are replaced by $D^{T,R}$'s. Thus, Hall-like temperature and concentration gradients are generated, which are transverse to the dissipative heat and concentration currents, respectively.

3.4.4 Viscosity

As the third example we consider field dependent generalizations of the viscosity tensor

$$\begin{aligned}
\nu_{ijkl}^R(H) &= \nu_1^R[\epsilon_{imp}n_jn_kn_l + \epsilon_{jmp}n_in_kn_l - \epsilon_{kmp}n_jn_in_l \\
&\quad -\epsilon_{lmp}n_jn_kn_i]\, n_pH_m \\
&+ \nu_2^R[\epsilon_{jmp}n_l\delta_{ik} - \epsilon_{lmp}n_j\delta_{ik} + \epsilon_{jmp}n_k\delta_{il} \\
&\quad -\epsilon_{kmp}n_j\delta_{il} + \epsilon_{imp}n_k\delta_{jl} - \epsilon_{kmp}n_i\delta_{jl} \\
&\quad +\epsilon_{imp}n_l\delta_{jk} - \epsilon_{lmp}n_i\delta_{jk}]\, n_pH_m \\
&+ \nu_3^R[\epsilon_{kmp}n_l\delta_{ij} + \epsilon_{lmp}n_k\delta_{ij} \\
&\quad -\epsilon_{imp}n_j\delta_{kl} - \epsilon_{jmp}n_i\delta_{kl}]\, n_pH_m \\
&+ \nu_4^R[\epsilon_{ikp}n_jn_l + \epsilon_{ilp}n_jn_k \\
&\quad +\epsilon_{jlp}n_in_k + \epsilon_{jkp}n_in_l]\, n_pn_mH_m \\
&+ \nu_5^R[\epsilon_{ikp}n_jn_l + \epsilon_{ilp}n_jn_k + \epsilon_{jlp}n_in_k + \epsilon_{jkp}n_in_l]\, H_p \\
&+ \nu_6^R[\epsilon_{ikp}\delta_{jl} + \epsilon_{ilp}\delta_{jk} + \epsilon_{jlp}\delta_{ik} + \epsilon_{jkp}\delta_{il}]\, n_pn_mH_m \\
&+ \nu_7^R[\epsilon_{ikp}\delta_{jl} + \epsilon_{ilp}\delta_{jk} + \epsilon_{jlp}\delta_{ik} + \epsilon_{jkp}\delta_{il}]\, H_p \\
&+ \nu_8^R n_p[\epsilon_{ikp}(H_jn_l + H_ln_j) + \epsilon_{ilp}(H_jn_k + H_kn_j) \\
&\quad +\epsilon_{jlp}(H_in_k + H_kn_i) + \epsilon_{jkp}(H_in_l + H_ln_i)]
\end{aligned} \tag{3.36}$$

Because of $\nu^R_{ijkl}(H) = \nu^R_{jikl}(H)$ and $\nu^R_{ijkl}(H) = \nu^R_{ijlk}(H)$ the stress tensor remains symmetric and (3.36) does not contain any coupling to the vorticity. All contributions in (3.36) are reversible, where the antisymmetry w.r.t. exchange of the first pair of indices with the second one, $\nu^R_{ijkl}(H) = \nu^R_{klij}(-H) = -\nu^R_{klij}(H)$, (according to Onsager's relation) guarantees zero entropy production. The major effect of these new terms is that a density wave (sound wave) is not only connected to div$\boldsymbol{v}$, but also to transverse velocities (and thus to all other variables). This will be manifest as (reversible) bulk shear stresses accompanying the sound wave. For example, for a density wave with amplitude $\Delta\rho$, frequency ω and wave vector k along the x-direction, magnetic field H along the y-direction, this bulk shear stress will be felt by a tracer particle as a transverse force

$$f_z = \bar{\nu}^R \, \omega \, k \, H \, \frac{\Delta\rho}{\rho_0} \tag{3.37}$$

with $\bar{\nu}^R = 2\nu^R_2 + \nu^R_3 - 2\nu^R_7$, $\bar{\nu}^R = \nu^R_1 + 2\nu^R_2 - \nu^R_3 - 2\nu^R_5 - 2\nu^R_7$, and $\bar{\nu}^R = -2\nu^R_6 - 2\nu^R_7$ if $\boldsymbol{n}$ is along the z-, x- and the y-direction, respectively.

3.4.5 Director reorientation

In eq.(3.7) the rotational viscosity $\gamma_0^{-1}\delta^\perp_{ij} \equiv (\gamma^{-1})_{ij}$ acquires linear field-dependent additions

$$(\gamma^{-1})^R_{ij}(H) \;=\; \frac{1}{\gamma^R_1}\epsilon_{ijk}n_k n_p H_p + \frac{1}{\gamma^R_2}(\epsilon_{ijp} + \epsilon_{ipk}n_k n_j - \epsilon_{jpk}n_k n_i)H_p \tag{3.38}$$

which are reversible and give zero entropy production, because they are antisymmetric in i and j according to Onsager's relation. Of course, they are also transverse to $\boldsymbol{n}$ in both indices $n_i\,(\gamma^{-1})^R_{ij}(H) = 0 = n_j\,(\gamma^{-1})^R_{ij}(H)$.

Usually, the so-called rotational viscosity γ_0 is measured by the homogeneous relaxation of the director towards an external magnetic field due to the magnetic anisotropy effect (3.24). In this case $\boldsymbol{H}$ and $\boldsymbol{n}(t)$ lie in the same plane all the time with relaxation rate $(\chi_a/\gamma_0)H^2$ [29]. The new terms in (3.38) change this picture. With (3.24,3.38) the director relaxation equation (3.3) takes the form

$$\dot{n}_i = \chi'_a \delta^\perp_{ij} H_j(\boldsymbol{H}\cdot\boldsymbol{n}) + \chi''_a(\boldsymbol{H}\times\boldsymbol{n})_i(\boldsymbol{H}\cdot\boldsymbol{n})^2 \tag{3.39}$$

where $\chi'_a = \chi_a/\gamma_0$ and $\chi''_a = \chi_a(1/\gamma^R_1 + 1/\gamma^R_2)$. Obviously, $\boldsymbol{n}(t)$ does not stay in the (initial) plane given by $\boldsymbol{H}$ and $\boldsymbol{n}(0)$, since there is a nonvanishing component $(\boldsymbol{H}\times\boldsymbol{n})\cdot\dot{\boldsymbol{n}}$ in (3.39). Thus, there are two distinct and coupled dynamic processes involved. For small angles the solutions of (3.39) can be written

$$\begin{aligned} \varphi &= \varphi_0 \exp(-\chi'_a H^2 t)\cos(\chi''_a H^3 t) \\ \theta &= \varphi_0 \exp(-\chi'_a H^2 t)\sin(\chi''_a H^3 t) \end{aligned} \tag{3.40}$$

where φ is the angle between the field and the projection of $\boldsymbol{n}(t)$ onto the initial plane $\boldsymbol{H}/\boldsymbol{n}(0)$ and θ is the angle of $\boldsymbol{n}(t)$ with this initial plane. The time dependence of φ is not a simple exponential decay, but shows an oscillation about it. The angle θ describes spatial oscillations of the director during the reorientation process. With field reversal $\boldsymbol{H} \to -\boldsymbol{H}$, also θ changes sign. Without the new reversible terms ($\chi''_a = 0$) a simple relaxation for φ, which is then the true angle between $\boldsymbol{n}$ and $\boldsymbol{H}$ is regained.

3.5 Summary

In this chapter we have derived hydrodynamic equations for ferronematics in the limit that the magnetic degree of freedom has relaxed to its equilibrium value. When comparing the equations derived here with the usual description of ordinary nematic liquid crystals, we find that there is no additional contribution to the static behavior linear in the magnetic field. This situation changes completely, however, when one investigates dynamic coupling terms between the various hydrodynamic variables that are linear in the magnetic field.

The new dynamic effects predicted here come in four classes. In most nematics, for temperatures far above a smectic phase, one observes the phenomenon of flow alignment. A shear flow applied to a spatially homogeneous director field leads to a stationary configuration in which the director includes an angle with its original orientation - the flow alignment angle. In the case of usual nematics the director lies in the shear plane. Here we predict that an additional magnetic field *in* the shear plane applied to a ferronematic forces the director *out* of the shear plane due to the dynamic effects given here, which couple the director to the shear flow dissipatively.

Applying a temperature gradient to a nematic leads to a heat flux that has components parallel to the applied temperature gradient and parallel to the director. Here we suggest that an additional magnetic field orthogonal to the temperature gradient applied to a ferronematic leads to an additional reversible heat current that is perpendicular to both, the applied magnetic field and the temperature gradient.

In most hydrodynamic systems including ordinary nematics only viscous effects couple the various components of the velocity field. For a ferronematic there are, in addition, several terms coupling the three components of the velocity field reversibly. One of the consequences of these new contributions could be detected experimentally studying the effect of a sound wave propagating in $x-$direction, say, on a tracer particle also exposed to a magnetic field in $y-$direction. For this configuration we predict the occurrence of a force on this tracer particle in $z-$ direction, that is perpendicular to the plane spanned by the two applied fields.

Director reorientation is expected to change as well when switching from an ordinary nematic to a ferronematic. Here we have shown that the director reorientation picks up reversible contributions in addition to the usual director diffusion associated with the rotational viscosity γ_1. The new reversible contributions are predicted to lead to a relaxation oscillation when the director is reoriented in an external magnetic field in contrast to the simple relaxation observed for usual nematics.

Chapter 4

Macroscopic dynamics of ferronematics with the magnetization as an independent variable[‡]

4.1 Introduction

In ferrofluids the magnetization (its orientation as well as its absolute value) relaxes to the equilibrium value set by the external field. The appropriate relaxation time is much larger than all microscopic time scales and can be relevant for the macroscopic dynamics, particularly in complicated lyotropic systems [9]. In this case one should treat the magnetization as an additional dynamic variable with its own dynamical (relaxation) equation. For isotropic ferrofluids this has been done in [39] and within a hydrodynamic description quite recently in [40].

In ferronematics the orientations of the director and the magnetization are linked in equilibrium, but the dynamics off equilibrium can be quite different: an external field reorients the magnetization quite easily due to the superparamagnetic effect, but is less effective regarding the director, which only is coupled to the magnetic field by the diamagnetic anisotropy effect. Vice versa, an electric field strongly orients the director but not the orientation of the magnetization. Thus, it is easy to create situations, where the director and the magnetization are quite different and where they relax independently into their equilibrium orientation. We also keep the absolute value of the magnetization as a relevant variable, but not the degree of nematic order, since the latter is not specifically influenced by a magnetic field or by the magnetic degrees of freedom and, thus, behaves as in ordinary nematics (and is relevant near the isotropic phase transition, only).

For ferronematics hydrodynamic equations were derived (chapter 3) in the limit that the magnetic degree of freedom has already relaxed to its equilibrium value. Here we generalize the set of hydrodynamic equations for ferronematics (in a constant external magnetic field) by including the magnetization as an additional, slowly relaxing variable. Special emphasis is laid on the static (Sec.4.2) and dynamic (Sec.4.3) cross-couplings between the nematic and the magnetic degrees of freedom. As examples for their relevance, and possible ways for measuring such effects, we discuss in more detail sound propagation and damping (Sec.4.4) as well as the

[‡]This chapter is based on ref. [38]

rheology during shear flow (Sec.4.5).

In Ref. [41] an extended description of electromagnetic effects in nematic liquid crystals has been given within the framework of generalized dissipative Maxwell equations. A non-hydrodynamic magnetic degree of freedom (a generalized dissipative magnetic field) is introduced, the dynamics of which can be compared to the dissipative part of our magnetization dynamics, while there is no counterpart in [41] to the reversible dynamics of an independent magnetization degree of freedom (see below).

4.2 Statics and thermodynamics

The macroscopic description of a system starts with the identification of the relevant variables. Apart from the quantities that are related to local conservation laws, like mass density (ρ), momentum density ($\boldsymbol{g}$), energy density (ε) and concentration (c) of the magnetic particles[1] or that are related to spontaneously broken continuous symmetries like reorientations of the director $\boldsymbol{n}$, we take, as discussed in the introduction, the magnetization $\boldsymbol{M}$ as slowly relaxing variable. To take into account Maxwell's equations the magnetic induction $\boldsymbol{B}$ must be considered as well. According to the Eulerian description all variables are local fields, i.e. volume densities that depend on space and time. The director $\boldsymbol{n}$ is a unit vector and due to the special nematic symmetry all equations have to be invariant under the replacement $\boldsymbol{n} \to -\boldsymbol{n}$. The magnetization $\boldsymbol{M} = M\boldsymbol{m}$ is associated with rotations $\delta\boldsymbol{m}$ as well as changes in the absolute value δM.

Assuming local thermodynamic equilibrium, i.e. all other, fast relaxing quantities are already in equilibrium, the Gibbs relation

$$d\varepsilon = Td\sigma + \mu d\rho + \mu_c dc + v_i dg_i + H_i dB_i + h_i^M dM_i + h_i^{n\prime} dn_i + \Phi_{ij} d(\nabla_j n_i) \tag{4.1}$$

connects the macroscopic variables to the entropy density σ. In eq.(4.1) the thermodynamic quantities: chemical potential (μ), temperature (T), relative chemical potential (μ_c), nematic molecular fields (Φ_{ij}, $h_i^{n\prime}$), velocity (v_i), magnetic Maxwell field (H_i) and the magnetic molecular field (h_i^M) are defined as partial derivatives of the energy density with the respect to the appropriate variables [34].

In equilibrium the magnetization is generally a nonlinear function of the external field. This function is known from experiments [42] or from simulations [43]. The equilibrium value of the magnetization, $\boldsymbol{M}_0$ at a given external field, which may have a field independent part in case of true ferromagnetism, is an input parameter into our dynamic theory. In addition, we assume the equilibrium orientation of the director to be parallel to the field (and the equilibrium magnetization). The case of a perpendicular director alignment is discussed in Sec.4.6.

The statics, i.e. the relation between the conjugate quantities and the variables, is conveniently set up by providing an energy density function, usually in harmonic approximation (bilinear in the variables). We will do here the same for the magnetic part of the energy density and consider below the more general description. Thus $\varepsilon = \varepsilon_n + \varepsilon_M$ with the magnetic energy

[1] In lyotropic systems one could also take into account additionally the concentration of the solvent c_S without changing the major results, since it has the same transformation behavior as c and thus makes the same type of coupling terms.

density

$$\varepsilon_M(\boldsymbol{B},\boldsymbol{M}) \;=\; \frac{B^2}{2} - \boldsymbol{M}\cdot\boldsymbol{B} + \frac{1}{2}A_1\left(\boldsymbol{n}\cdot\boldsymbol{M}\right)^2 + \frac{1}{2}A_2\boldsymbol{M}^2 \tag{4.2}$$

and ε_n the energy density of a conventional nematic liquid crystal [34] (without magnetization and external field). The term $\frac{1}{2}A_1\left(\boldsymbol{n}\cdot\boldsymbol{M}\right)^2$ describes the coupling between the nematic director and the magnetic particles. This strong interaction was observed in a series of experiments [15, 17, 20] studying the Fredericks transition in ferronematics. For $\boldsymbol{n}\parallel\boldsymbol{M}$ being the energy minimum, A_1 has to be negative. Generally the coefficients $A_{1,2}$ are functions of the state variables, like temperature, pressure etc., but also of $\boldsymbol{M}_0^2$ (or the external field strength). Only for a linearized description, valid for small deviations from equilibrium, are the coefficients constant.

Using eq.(4.2), the magnetic Maxwell field H_i is defined in the usual way

$$H_i = \left(\frac{\partial\varepsilon}{\partial B_i}\right)_{\boldsymbol{M},\boldsymbol{n},\ldots} = B_i - M_i, \tag{4.3}$$

while the magnetic molecular field h_i^M reads

$$h_i^M = \left(\frac{\partial\varepsilon}{\partial M_i}\right)_{\boldsymbol{B},\boldsymbol{n},\ldots} = -B_i + A_1 n_i n_j M_j + A_2 M_i \tag{4.4}$$

Note that because of the definition (4.3), it is not possible to have a direct coupling between the external field $\boldsymbol{B}$ and the director; the field orientation of the director is mediated by the magnetization via the term $\sim A_1$.

In equilibrium h_i^M has to be zero and $B_i = A_1 n_i n_j M_j + A_2 M_i$ results. With that solution the magnetic energy density (4.2) can be expressed as $\varepsilon_M(\boldsymbol{B}) = \frac{1}{2}H_i(\boldsymbol{B})B_i$. In the regime of linear magnetism or if linearized for small deviations from equilibrium, one can use instead the usual magnetic susceptibility tensors, defined by $B_i = \mu_{ij}H_j$ and $M_i = \chi_{ij}H_j$, which both have the uniaxial form $\mu_{ij} = \mu_\perp\delta_{ij}^{tr} + \mu_\parallel n_i n_j = \mu_\perp\delta_{ij} + \mu_a n_i n_j$ (where $\delta_{ij}^{tr} = \delta_{ij} - n_i n_j$ is the transverse Kronecker symbol). Comparison with the equilibrium solution of (4.4) gives $A_1 = \mu_\parallel/\chi_\parallel - \mu_\perp/\chi_\perp$ and $A_2 = \mu_\perp/\chi_\perp$. Written in this way the magnetic energy density (4.2) obtains the familiar form $\varepsilon_M(\boldsymbol{B}) = \frac{1}{2}\mu_{ij}H_iH_j$. In the general case, again, the magnetic susceptibilities are not constants, but depend on the magnetization or the external field.

In ordinary nematic liquid crystals instead of $\varepsilon_M(\boldsymbol{B})$ usually the Legendre-transformed energy $\varepsilon_M(\boldsymbol{H}) = \varepsilon_M(\boldsymbol{B}) - \boldsymbol{B}\cdot\boldsymbol{H}$ is used, for which we get the well-known form $2\varepsilon_M(\boldsymbol{H}) = -\chi_a(\boldsymbol{n}\cdot\boldsymbol{H})^2 - (\chi_\perp - 1)\boldsymbol{H}^2$ where very often the vacuum field energy ($\boldsymbol{H}^2$) is omitted [29].

The molecular field $h_i^{n\prime}$

$$h_i^{n\prime} = \delta_{ij}^{tr}\left(\frac{\partial\varepsilon}{\partial n_j}\right)_{\boldsymbol{M},\boldsymbol{B},\ldots} = A_1\delta_{ij}^{tr}M_jM_kn_k \tag{4.5}$$

where higher order terms are neglected (3.20) and Φ_{ij} (3.19) can be combined to the field

$$h_i^n = \frac{\delta}{\delta n_i}\int\varepsilon dV = h_i^{n\prime} - \nabla_j\Phi_{ij}. \tag{4.6}$$

Since $\boldsymbol{n}$ is a unit vector that can only rotate, $n_i h_i^{n\prime} = 0$, which is ensured in (4.5) by the transverse Kronecker symbol. In equilibrium, $\boldsymbol{n} = const.$ and $\delta_{ij}^{tr} M_j = 0$, hence $h_i^n = 0$.

In the general case the equilibrium value of the magnetization $\boldsymbol{M^0}$ is a nonlinear function of an external magnetic induction $\boldsymbol{B}$, $M_i^0 = f_i(\boldsymbol{B})$. In isotropic ferrofluids simple theoretical models predict $\boldsymbol{f}(\boldsymbol{B}) = f(B)\boldsymbol{B}/B$ with $f(B)$ the Langevin function and $B = |\boldsymbol{B}|$. Actual experiments [42] and computer simulations [43] show a somewhat more complicated form for $f(B)$. We assume the function $\boldsymbol{f}(\boldsymbol{B})$ as known and given. To our hydrodynamic theory this is an input as are any other aspects of the equilibrium structure, e.g. the existence and the orientation of $\boldsymbol{n}$ w.r.t the external field. Assuming $\boldsymbol{f}(\boldsymbol{B})$ to be monotonous we can invert it and call it $\boldsymbol{g}(\boldsymbol{M}) = \boldsymbol{f}^{-1}(\boldsymbol{B})$. Using the same arguments as in Sec.4.2 one can construct the magnetic part of the energy density in the following form

$$\varepsilon(\boldsymbol{B}, \boldsymbol{n}, \boldsymbol{M}) = \frac{B^2}{2} - \boldsymbol{M}\cdot\boldsymbol{B} + \int (n_i n_j g_j^{(1)} + \delta_{ij}^{tr} g_j^{(2)}) dM_i \tag{4.7}$$

where, in contrast to the isotropic case, g_i has been decomposed into a longitudinal and a transverse part. This leads to

$$H_i = \left(\frac{\partial \varepsilon}{\partial B_i}\right)_{\boldsymbol{M},\boldsymbol{n},\ldots} = B_i - M_i \tag{4.8}$$

$$h_i^M = \left(\frac{\partial \varepsilon}{\partial M_i}\right)_{\boldsymbol{n},\boldsymbol{B},\ldots} = -B_i + n_i n_j g_j^{(1)} + \delta_{ij}^{tr} g_j^{(2)}. \tag{4.9}$$

In equilibrium the magnetic molecular field h_i^M is zero and $\boldsymbol{B} = \boldsymbol{g} \parallel \boldsymbol{n}$ (requiring $n_i n_j g_j = g_i^{(1)}$ and $\delta_{ij}^{tr} g_j^{(2)} = 0$ in equilibrium). Outside equilibrium $g_i(\boldsymbol{M}) \neq B_i$ and $\boldsymbol{n}$ is not parallel to $\boldsymbol{B}$, generally.

For the nematic molecular field

$$h_i^{n\prime} = \delta_{ij}^{tr}\left(\frac{\partial \varepsilon}{\partial n_j}\right)_{\boldsymbol{M},\boldsymbol{B},\ldots} = \delta_{ij}^{tr} n_k \int \Big(dM_j (g_k^{(1)} - g_k^{(2)}) + dM_k (g_j^{(1)} - g_j^{(2)}) \Big) \tag{4.10}$$

is found. Linearizing about equilibrium the choices $g_i^{(1)} = (A_1 + A_2) n_i n_j M_j$ and $g_i^{(2)} = A_2 \delta_{ij}^{tr} M_j$ lead back to eqs.(4.4,4.5).

4.3 Dynamics

The hydrodynamic equations for conserved, broken-symmetry and slowly relaxing variables are

$$\frac{\partial}{\partial t}\rho + div\,\rho\boldsymbol{v} = 0 \tag{4.11}$$

$$\frac{\partial}{\partial t}\sigma + div\,\sigma\boldsymbol{v} + div\boldsymbol{j}^{\boldsymbol{\sigma}} = \frac{R}{T} \tag{4.12}$$

$$\frac{\partial}{\partial t}g_i + \nabla_j\Big(v_j g_i + \delta_{ij}p + \sigma^{th}_{ij} + \sigma_{ij}\Big) = 0 \tag{4.13}$$

$$\Big(\frac{\partial}{\partial t} + v_j\nabla_j\Big)n_i + (\boldsymbol{n}\times\boldsymbol{\omega})_i + Y_i = 0 \tag{4.14}$$

$$\rho\Big(\frac{\partial}{\partial t} + v_j\nabla_j\Big)c + div\,\boldsymbol{j}^c = 0 \tag{4.15}$$

$$\Big(\frac{\partial}{\partial t} + v_j\nabla_j\Big)M_i + (\boldsymbol{M}\times\boldsymbol{\omega})_i + X_i = 0 \tag{4.16}$$

with

$$\sigma^{th}_{ij} = -B_jH_i - \frac{1}{2}(M_jh^M_i - M_ih^M_j) - \frac{1}{2}(n_jh^n_i - n_ih^n_j) + \Phi_{kj}\nabla_i n_k \tag{4.17}$$

where $\omega_i = \frac{1}{2}\epsilon_{ijk}\nabla_j v_k$ is the vorticity. The thermodynamic pressure p is given by

$$p = -\varepsilon + T\sigma + \mu\rho + \mu_c c + \boldsymbol{g}\cdot\boldsymbol{v} + \boldsymbol{B}\cdot\boldsymbol{H}. \tag{4.18}$$

The parts of the currents shown explicitly in (4.11-4.17) are not material dependent, but are given by general symmetry and thermodynamic principles [34], like transformation behavior under translations (convective terms) or rotations (e.g. $\ldots\times\boldsymbol{\omega}$) and by the requirement of zero entropy production ($R = 0$).

Using the relation [34] $\Omega_{ij}(-M_iB_j + h^M_iM_j + h^n_in_j + \Phi_{ki}\nabla_j n_k + \nabla_k(n_j\Phi_{ik})) = 0$, which is valid for any constant antisymmetric matrix $\Omega_{ij} = -\Omega_{ji}$ and which follows from the fact that the energy density (4.1) has to be invariant under constant rotation, eq.(4.17) can be transformed into

$$\sigma^{th}_{ij} = -\frac{1}{2}(B_jH_i + B_iH_j) + \frac{1}{2}(\Phi_{ki}\nabla_j n_k + \Phi_{kj}\nabla_i n_k) + \frac{1}{2}\nabla_k(n_j\Phi_{ik} - n_i\Phi_{jk}). \tag{4.19}$$

Here the antisymmetric part has the form of a divergence, which ensures angular momentum conservation. It can be brought into a manifestly symmetric form by some redefinitions [35].

The phenomenological parts of the entropy current j^σ_i, the stress tensor σ_{ij}, the concentration current j^c_i and the quasi-currents Y_i and X_i associated with the temporal changes of the director and the magnetization, respectively, are given below. The source term R/T in (4.12) is the entropy production, which is zero for reversible and positive for irreversible processes. The phenomenological part of the stress tensor σ_{ij} has to be symmetric guaranteeing angular momentum conservation.

Since we are not dealing with electromagnetic effects, we can use the static Maxwell equations to determine $\boldsymbol{B}$

$$curl\boldsymbol{H} = curl\,(\boldsymbol{B} - \boldsymbol{M}) = 0, \qquad div\boldsymbol{B} = 0. \tag{4.20}$$

The dynamic equation for the energy density follows from (4.11-4.16) via (4.1) and is not shown here.

The phenomenological currents written down in eqs.(4.11-4.16) can be split into dissipative (superscript D) and into reversible (superscript R) parts, depending on whether they give rise to a finite amount of dissipation ($R > 0$) or to a zero entropy production ($R = 0$). Using general symmetry and invariance arguments and the fact, that a magnetic field changes sign under time reversal, we obtain

$$\begin{aligned} j_i^{\sigma R} &= -\kappa_{ij}^R(M)\nabla_j T - D_{ij}^{TR}(M)\nabla_j \mu_c && (4.21)\\ j_i^{cR} &= -D_{ij}^R(M)\nabla_j \mu_c - D_{ij}^{TR}(M)\nabla_j T && (4.22)\\ \sigma_{ij}^R &= -\frac{1}{2}\lambda_{kji}h_k^n - c_{kij}^R(M)h_k^M - \nu_{ijkl}^R(M)A_{kl} && (4.23)\\ Y_i^R &= -\frac{1}{2}\lambda_{ijk}A_{jk} + (\gamma^{-1})_{ij}^R(M)h_j^n + \chi^R\left(\boldsymbol{n}\times\boldsymbol{h}^M\right)_i && (4.24)\\ X_i^R &= b_{ij}^R(M)h_j^M + \chi^R\left(\boldsymbol{n}\times\boldsymbol{h}^n\right)_i - c_{ijk}^R(M)A_{jk} && (4.25) \end{aligned}$$

with $A_{ij} = \frac{1}{2}\left(\nabla_i v_j + \nabla_j v_i\right)$. The magnetization-dependent tensors $\kappa_{ij}^R(M)$, $D_{ij}^R(M)$, $D_{ij}^{TR}(M)$, $(\gamma^{-1})_{ij}^R(M)$, $b_{ij}^R(M)$, $\nu_{ijkl}^R(M)$, $c_{ijk}^R(M)$ are all odd functions of the magnetization.

For the case of the magnetization already relaxed to its equilibrium value, similar tensors exist with M replaced by the external field H (except for b_{ij}^R and c_{ijk}^R). Their physical meaning has been discussed in chapter 3.

The second order tensors $D_{ij}^R(M)$, $D_{ij}^{TR}(M)$ and $b_{ij}^R(M)$ have the same form as the heat conduction tensor $\kappa_{ij}^R(M)$ (3.34), while the forms of $(\gamma^{-1})_{ij}^R(M)$ and $\nu_{ijkl}^R(M)$ are given in (3.38) and (3.36), respectively. The third rank tensor c_{ijk}^R describing a dynamic crosscoupling between flow and magnetization is symmetric in the two last indices and reads

$$\begin{aligned} c_{ijk}^R(M) &= c_1^R M_i n_j n_k + c_2^R(\delta_{ij}M_k + \delta_{ik}M_j) + c_3^R M_i\delta_{jk} + c_4^R n_i M_p n_p \delta_{jk}\\ &\quad + c_5^R(n_i M_j n_k + n_i M_k n_j) + c_6^R n_i M_p n_p n_j n_k \qquad (4.26) \end{aligned}$$

Such a coupling does not exist in isotropic ferrofluids, nor in conventional nematics.

Due to the new degree of freedom (magnetization) there is an additional term in the nematic quasi-current eq.(4.24) $\chi^R\left(\boldsymbol{n}\times\boldsymbol{h}^M\right)_i$ and a counter term in X_i^R, which describes a dynamic cross-coupling between magnetization and nematic director. It does not exist in ordinary nematics nor in isotropic ferrofluids. Its physical meaning (together with b_{ij}^R and c_{ijk}^R) will be explored in the Secs.4.4 and 4.5. The flow alignment tensor λ_{ijk} has the usual form [35] $\lambda_{ijk} = \lambda(\delta_{ij}^{tr}n_k + \delta_{ik}^{tr}n_j)$.

For the derivation of the dissipative parts of the phenomenological currents one usually expands the dissipation function R to second order in the thermodynamic forces and then obtains the dissipative currents by taking the variational derivatives with respect to the forces. We find for the dissipation function

$$\begin{aligned} R &= \frac{1}{2}\kappa_{ij}\left(\nabla_i T\right)\left(\nabla_j T\right) + \frac{1}{2}\nu_{ijkl}^D A_{ij}A_{kl} + \lambda_{ijk}^D(M)h_i^n A_{jk}\\ &+ \frac{1}{2}D_{ij}\left(\nabla_i\mu_c\right)\left(\nabla_j\mu_c\right) + \frac{1}{2}b_{ij}^D h_i^M h_j^M + c_{ijk}^D h_i^M A_{jk} + \chi_{ij}^D(M)h_j^M h_i^n\\ &+ \frac{1}{2\gamma_0}h_i^n\delta_{ij}^{tr}h_j^n + D_{ij}^T\left(\nabla_j T\right)\left(\nabla_i\mu_c\right) \qquad (4.27) \end{aligned}$$

Here ν^D_{ijkl} eq.(3.12) is the uniaxial viscosity tensor [35] and κ_{ij} eq.(3.10), D_{ij} and D^T_{ij} describe heat conduction, diffusion and thermodiffusion, respectively. Director diffusion or relaxation is given by one coefficient γ_0, while magnetization relaxation b^D_{ij} contains a transverse (rotational) and a longitudinal (absolute value) coefficient $b^D_{ij} = b^D_\perp \delta^{tr}_{ij} + b^D_\parallel n_i n_j$. All the 2nd rank field-free tensors mentioned above have this form. The meaning of λ^D_{ijk} has been discussed in chapter 3, while χ^D_{ij} will show up in Sec.4.5. The 3rd rank tensor c^D_{ijk} (4.50) again is specific to nematic ferrofluids and describes a dissipative coupling between flow and orientation of the magnetization.

The range of possible values of the coefficients in eq.(4.27) is restricted by the positivity of the entropy production.

The dissipative parts of the currents then read

$$
\begin{aligned}
j^{\sigma D}_i &= -\kappa_{ij}\nabla_j T - D^T_{ij}\nabla_j \mu_c && (4.28)\\
j^{cD}_i &= -D_{ij}\nabla_j \mu_c - D^T_{ij}\nabla_j T && (4.29)\\
\sigma^D_{ij} &= -\nu^D_{ijkl}A_{kl} - \lambda^D_{kij}(M)h^n_k - c^D_{kij}h^M_k && (4.30)\\
Y^D_i &= \frac{1}{\gamma_0}\delta^{tr}_{ij}h^n_j + \chi^D_{ij}(M)h^M_j + \lambda^D_{ijk}(M)A_{jk} && (4.31)\\
X^D_i &= b^D_{ij}h^M_j + \chi^D_{ji}(M)h^n_j + c^D_{ijk}A_{jk} && (4.32)
\end{aligned}
$$

The dissipative second rank tensor χ^D_{ij} is different from the reversible ones (determined above), since it has to contain an odd number of $\boldsymbol{n}$'s

$$\chi^D_{ij}(M) = \chi^D_1 \delta^{tr}_{ik} M_k n_j + \chi^D_2 \delta^{tr}_{ij} M_k n_k \qquad (4.33)$$

This set of equations is comparable to the dissipative dynamics given in [41] for the magnetic and nematic degrees of freedom. Interpreting $-H^D_i$ as our current X^D_i and $c\,\mathrm{curl}\boldsymbol{E}^0$ as our conjugate $\boldsymbol{h}^M$, eq.(13) of [41] is compatible with eqs. (4.30-4.32) in the uniaxial case ($\boldsymbol{n} \parallel \boldsymbol{m}$ in equilibrium). There is however no counterpart in [41] to the reversible dynamics of eqs.(4.23-4.25).

4.4 Propagation of sound

In this section we derive the longitudinal eigenmodes (sound) of the system with the nematic director $\boldsymbol{n}^0$ parallel to the magnetic field in equilibrium. In ordinary nematics the sound velocity is isotropic and does not depend on the external field, since the nematic orientational fluctuations do not couple to sound. Only sound damping is anisotropic due to the anisotropy of viscosity and heat conduction. In nematic ferrofluids with the magnetization relaxed to its equilibrium value $\boldsymbol{M}_0$, sound is accompanied by transverse forces (chapter 3), but the sound velocity is still isotropic and field-independent. Here we focus on the effect of the new variable (magnetization) on the sound spectrum. Thus, we can neglect all diffusional processes connected e.g. with viscosity and heat conduction as well as their reversible counterparts. Only the relaxations of the director and the magnetization in the field are kept. The relevant linearized static fields are then

$$
\begin{aligned}
h^{n\prime}_i &= A_1 M_0 \delta M_i - A_1 {M_0}^2 \delta n_i && (4.34)\\
h^M_i &= -\delta B_i + A_1 M_0 \delta n_i + A_2 \delta M_i + A_1 n^0_i n^0_j \delta M_j && (4.35)
\end{aligned}
$$

with n_i^0 the unit vector along the field. Assuming a one-dimensional plane wave the space-time dependence is $\sim \exp i(-\omega t + \boldsymbol{k}\cdot\boldsymbol{r})$ for all deviations from equilibrium and the linearized set of dynamic equations becomes an algebraic one. Even then the full system of equations is rather complicated in the case of ferronematics. It can be simplified by looking at particular geometries.

Let us consider sound in the case where the external magnetic field, the equilibrium magnetization, and the director are perpendicular to the wave vector. Field fluctuations δB_i are fixed by the static Maxwell equations (4.20) to $\delta B_i = \delta M_j(\delta_{ij} - k_i k_j k^{-2})$. However, since $A_2 \gg 1$ (because of $\chi_\perp \ll 1$), this contribution can safely be neglected in (4.35). Then there are only three relevant variables left, the density ρ, the longitudinal velocity component ($\boldsymbol{v} \parallel \boldsymbol{k}$) and the (longitudinal) component $\delta\boldsymbol{M} \parallel \boldsymbol{B}$, which is transverse to $\boldsymbol{k}$, changing the sound dispersion relation into

$$\frac{\omega^2}{k^2} - c_0^2 = \frac{\mu_\parallel}{\rho}(c_3^R + c_4^R)^2 \chi_\parallel H^2 \frac{i\omega}{i\omega - \tau} \tag{4.36}$$

with c_0 the usual adiabatic sound velocity and $\tau = b_\parallel^D \mu_\parallel / \chi_\parallel$ the relaxation time of the longitudinal magnetization. Here B^2 has been replaced by $(\chi_\parallel H)^2$ and $A_1 + A_2$ by $\mu_\parallel / \chi_\parallel$. The coefficient c_3^R (4.26) also exists in isotropic ferrofluids. Thus, this change in the sound dispersion relation is possible in the isotropic phase as well [44].

If the sound period is much bigger than the inverse relaxation time of the magnetization $kc_0 \gg 1/\tau$, there is a field dependent addition to the sound velocity, while in the opposite, realistic case $kc_0 \ll 1/\tau$, there is a field-dependent sound damping due to magnetization relaxation

$$\mathfrak{Im}(\omega) = -\frac{1}{2}\frac{(c_3^R + c_4^R)^2}{\rho b_\parallel^D}\chi_\parallel^2 H^2 k^2 \tag{4.37}$$

that comes in addition to the usual magnetic-field-independent sound damping (not shown here). This effect can be used to measure the combination $c_3^R + c_4^R$ of new coefficients by varying the external field. In the case of sound waves along the field direction ($\boldsymbol{k} \parallel \boldsymbol{B}$) the situation is quite similar, only a different combination of transport parameters is involved, i.e. in (4.36,4.37) $c_3^R + c_4^R$ has to be replaced by $c_1^R + 2c_2^R + c_3^R + c_4^R + 2c_5^R + c_6^R$. A completely different situation arises, when the sound is oblique to the field $\boldsymbol{B}$ (i.e. $\boldsymbol{k}$ has an angle different from zero or π with $\boldsymbol{B}$). Then the longitudinal variables $div\boldsymbol{v}$, $\delta\rho$, and $\boldsymbol{B}\cdot\delta\boldsymbol{M}$ are coupled to the transverse ones ($curl\boldsymbol{v}$, $\delta_{ij}^{tr}\delta M_j$, δn_i) mainly through the existence of the tensor $c_{ijk}^R(M)$ (4.23, 4.25, 4.26). This has the consequence that shear flow is connected to sound and vice versa, and if one excites one of them the other is excited as well. A similar phenomena for isotropic ferrofluids is discussed in [44].

The picture is qualitatively similar for the biaxial case ($\boldsymbol{n} \perp \boldsymbol{B}$). When the sound is along the preferred directions (either parallel to $\boldsymbol{n}$, to $\boldsymbol{B}$ or perpendicular to both) the sound dispersion gets an extra field dependent damping similar to (4.37), while in the oblique case again sound is coupled to shear flow.

4.5 Rheology

To evaluate the influence of the static and dynamic coupling between the nematic degree of freedom and the magnetization we investigate the stress induced by applying a shear flow

that varies periodically in time. To make the problem simpler we consider the particular geometry, where the equilibrium orientation of the nematic director and the magnetization are perpendicular to the flow direction and along the gradient direction. The linear response of the system that contains information on the material properties is described by the frequency dependent response function $G(\omega)$, which is defined as the ratio of the induced stress (say σ_{xz}) to the applied "strain" $e_{xz} \equiv iA_{xz}/\omega$

$$G(\omega) = \frac{\sigma_{xz}}{e_{xz}} = G'(\omega) + iG''(\omega), \tag{4.38}$$

which has poles at the frequencies of those eigenmodes that couple to shear flow. The real part G' (imaginary part G'') describes the reversible, in-phase (irreversible, out-of-phase) response. When calculating $G(\omega)$ the flow is assumed to show the undisturbed, externally imposed linear profile.

The relaxation process of the magnetization to its equilibrium value is fast in comparison to the nematic director relaxation/diffusion time. This gives the possibility to investigate the influence of the nematic-magnetization couplings on the two modes separately. Since the slow nematic mode seems to be more convenient for experiments, we will concentrate on this mode in the following. We consider the situation without an external magnetic field first and then the much more complicated case with a field (along the gradient direction). This probes the coupled dynamics of the transverse variables ($curl\boldsymbol{v}$, $\delta^{tr}_{ij}\delta M_j$, δn_i).

The response function without magnetic field has the following form

$$\frac{G'}{\omega^2} = \frac{C\Gamma}{\omega^2 + \Gamma^2} \tag{4.39}$$

$$\frac{G''}{\omega} = \nu_3 - \frac{\xi_1}{q_1} + \frac{C\omega^2}{\omega^2 + \Gamma^2}, \tag{4.40}$$

with

$$\xi_1 = \frac{1-\lambda^2}{4} + \frac{(c^D)^2}{b^D_\perp \gamma_0} - \frac{c^D \chi^R \lambda}{b^D_\perp} \tag{4.41}$$

$$q_1 = \frac{1}{\gamma_0} + \frac{(\chi^R)^2}{b^D_\perp} \tag{4.42}$$

$$C = \frac{\xi_1}{q_1} - \frac{(c^D)^2}{b^D_\perp} = \frac{1}{q_1}\Big(\frac{1}{4} - \big[\frac{\lambda}{2} + \frac{c^D\chi^R}{b^D_\perp}\big]^2\Big) \tag{4.43}$$

$$\Gamma = q_1 K_3 k^2 \tag{4.44}$$

eqs.(4.39, 4.40) are, as discussed above, only applicable for low frequencies with $\omega \ll A_2 b^D_\perp$. In the loss modulus G'' the apparent Newtonian shear viscosity differs from the bare shear viscosity ν_3 by $-\xi_1/q_1$ where $1/q_1$ (4.42) is the renormalized nematic orientational viscosity that deviates from γ_0 due to the reversible dynamic crosscoupling (χ^R) between director and magnetization (4.24,4.25), and the transverse magnetization relaxation $b^D_\perp$. The new contribution $\sim \xi_1$ is due to the relaxation of the magnetization ($b^D_\perp$) and of the director (γ_0), as well as due to the dissipative crosscoupling between flow and magnetization (c^D) and the reversible crosscouplings of the director with flow (λ) and magnetization (χ^R). This change in the apparent viscosity is

absent in isotropic ferrofluids, but present in ordinary nematics (for $\lambda \neq \pm 1$). However, since ferronematics, ordinary nematics and isotropic ferrofluids are different phases with generally different (bare) viscosities, the additional change of the viscosity due the magnetization degree of freedom is only a quantitative effect and probably difficult to observe. There are, however, magnetic oscillations (around $M = 0$) induced by the periodic shear flow (directly via c^D) or mediated by director oscillations (via χ^R and λ). The oscillating magnetization points out of the shear plane with a peak amplitude that has its maximum for $\omega \approx \Gamma$. Such magnetic oscillations can be measured by a Hall probe.

Qualitatively new, compared to isotropic ferrofluids, is the occurrence of a director diffusional mode in G' and G'' with amplitude C (4.43) and width Γ (4.44). The amplitude C shows that, even without a magnetic field, the magnetization as an independent variable with its own dynamics influences the relaxation process of the director. However this mode has its strongest influence at $\omega \approx \Gamma$, which is very low, if the wave vector k is small, and it may be hard to detect experimentally. Therefore we also study the case with an external field, where not only the relevant frequencies are shifted to higher values, but where also another, qualitatively new behavior is seen. Indeed we find

$$\begin{aligned} \frac{G'}{\omega} &= \frac{1}{2Mq_2}\left(\frac{\Omega^2\xi_1 - \Omega M q_2\xi_2 + {q_1}^2\xi_1}{\left(\Omega - q_2 M\right)^2 + \left(q_1 - M^2 q_3\right)^2}\right. \\ &\qquad \left. - \frac{\Omega^2\xi_1 + \Omega M q_2\xi_2 + q_1^2\xi_1}{\left(\Omega + q_2 M\right)^2 + \left(q_1 - M^2 q_3\right)^2}\right) \qquad (4.45) \\ \frac{G''}{\omega} &= \nu_3 - \frac{1}{2Mq_2}\left(\frac{\Omega^3\xi_3 - \Omega^2 M\xi_3 q_2 + \Omega {q_1}^2\xi_3 + M q_2 q_1\xi_1}{\left(\Omega - q_2 M\right)^2 + \left(q_1 - M^2 q_3\right)^2}\right. \\ &\qquad \left. - \frac{\Omega^3\xi_3 + \Omega^2 M\xi_3 q_2 + \Omega {q_1}^2\xi_3 - M q_2 q_1\xi_1}{\left(\Omega + q_2 M\right)^2 + \left(q_1 - M^2 q_3\right)^2}\right) \qquad (4.46) \end{aligned}$$

where $\Omega \equiv \omega/(K_3 k^2 + \chi_a H^2)$ is the scaled frequency and $M = \chi_\parallel H$. The abbreviations $q_{2,3}$

$$q_2 = \frac{1}{\gamma_1^R} + \frac{1}{\gamma_2^R} + \frac{2\chi_2^D\chi^R}{b_\perp^D} - \frac{(\chi^R)^2}{(b_\perp^D)^2}(b_1^R + b_2^R) \qquad (4.47)$$

$$q_3 = \frac{1}{(b_\perp^D)^3}\left(\chi_2^D b_\perp^D - \chi^R(b_1^R + b_2^R)\right)^2 \qquad (4.48)$$

are combinations of the various static susceptibilities and the transport parameters involved, while $\xi_2 = \xi_1 + q_1\xi_3$, and $\xi_3 = (c^D)^2/b_\perp^D$ with ξ_1 and q_1 given in (4.41,4.42), respectively. Since we concentrate on the frequency dependence here, we have suppressed some additional M^2-dependences of ξ_{1-3} and q_2, which would render the results (4.45,4.46) extremely involved.

In the presence of an external field the relaxation mode is much more complicated than without a field. The most important, and experimentally most easily detectable feature is the shift of the nematic pole to finite frequencies $\Omega = \pm q_2 M$ (cf. Fig.4.1). The existence of q_2 is characteristic for nematic ferrofluids, since neither the reversible coupling between director and magnetization rotations (χ^R), nor the reversible counterparts to director diffusion/relaxation ($\gamma_{1,2}^R$) and magnetization relaxation ($b_{1,2}^R$) exist in ordinary nematics or isotropic ferrofluids. For the true frequency ω the shift increases $\sim H^3$ for fields larger than $\sqrt{K_3 k^2/\chi_a}$. In an oscillating Couette shear experiment, under the approximation of a linear velocity profile, this behavior

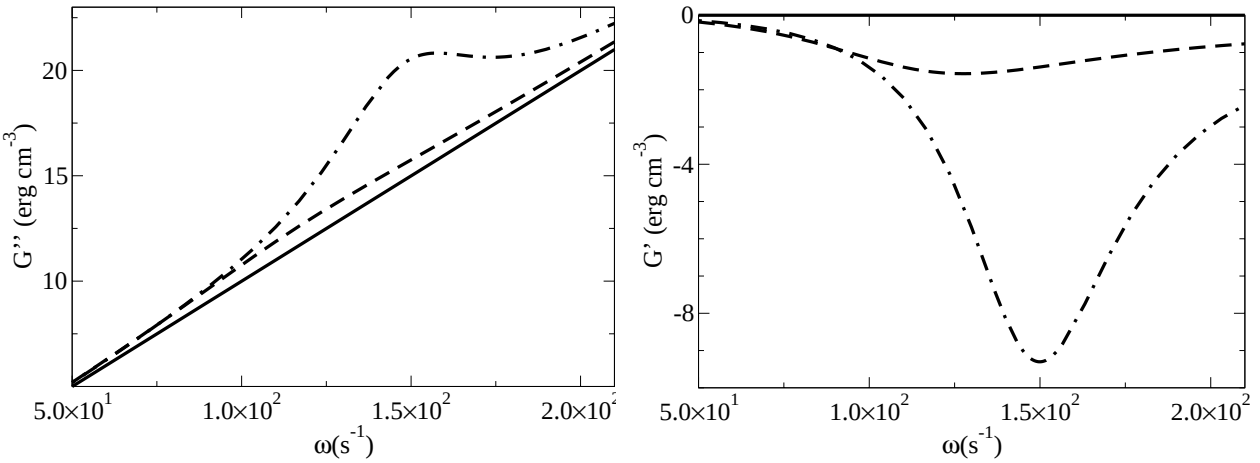

Figure 4.1: G'' (left) and G' (right) as functions of the frequency for increasing magnetic field strengths: $H = 0$ (solid), $H = 320G$ (dashed), and $H = 350G$ (dash-dotted); in our rationalized Gaussian unit system (cf. eq.(4.2)) $1G^2 = (1/4\pi) erg\, cm^{-3}$. The values of the parameters were taken to be $\gamma_0 = 10^{-1}\, g\, s^{-1} cm^{-1}$, $K_3 = 10^{-6}\, dyn$, $k = 100 cm^{-1}$, $\nu_3 = 10^{-1}\, g\, s^{-1} cm^{-1}$, $\chi_a = 10^{-4}$, $\chi_{\parallel} = 10^{-4}$, $\chi^R = 3\, s^{-1} G^{-1}$, $\chi_2^D = 3\, cm\, s\, g^{-1}$, $b_\perp^D = 1\, s^{-1}$, $b_1^R + b_2^R = 40\, G^{-1} s^{-1}$, $c^D = 7 \times 10^{-3}\, G$, $(1/\gamma_1^R) + (1/\gamma_2^R) = 1\, s\, cm\, g^{-1} G^{-1}$, and $\lambda = 1$ (to eliminate ordinary nematic effects). On this scale the zero field effects (4.39,4.40) can hardly be seen.

can be measured. There is also the possibility that the nematic orientational mode becomes propagating for some intermediate fields strengths, if $q_2 M > q_1 - M^2 q_3$. As in the field-free case the oscillating shear flow induces also magnetization oscillations, but with a field there are oscillating components not only out of the shear plane, but also along the flow direction.

4.6 The biaxial case

In this section we deal with the case that in equilibrium the nematic director $\boldsymbol{n}^0$ is perpendicular to the external field $\boldsymbol{B}$ (and the magnetization $\boldsymbol{M}_0$). This case is often realized in lyotropic systems [17]. In the plane perpendicular to the field the direction of $\boldsymbol{n}$ is not specified, i.e. the rotational in-plane symmetry is spontaneously broken and the system is biaxial. Thus, there is one rotation of $\boldsymbol{n}$ (the in-plane rotation) that is hydrodynamic (diffusive), while the out-of-plane rotation is relaxing (non-hydrodynamic) due to the external field. This difference to the uniaxial case discussed in the main body of this manuscript (where both rotations of $\boldsymbol{n}$ are relaxing) becomes apparent in the statics, i.e. in the magnetic energy of the system and hence in the molecular fields h_i^M and $h_i^{n\prime}$.

The static equations (4.2-4.6) still apply, however with $A_1 > 0$ ensuring $\boldsymbol{n}^0 \perp \boldsymbol{M}_0$. The linearized expressions (4.4,4.5) for $h_i^{n\prime}$ and h_i^M now only contain the out-of-plane components of $\boldsymbol{n}$ ($M_k \delta n_k$), while the in-plane component appears in the gradient part Φ_{ij} only.

The form of the dynamic equations is not affected. Only the material tensors have a more complicated form (containing more coefficients generally) due to the lower orthorhombic

symmetry. We will give the biaxial form of the field-free material tensors, while those that have to contain an odd number of factors $\boldsymbol{M}$ have been given above (for the uniaxial as well as the biaxial case to linear order in $\boldsymbol{M}$). In the biaxial case we have to discriminate between the directions of the director and the magnetization, which we denote by its unit vector $\boldsymbol{m} = \boldsymbol{M}/M$. The form of the material tensors of usual biaxial nematics is given in [45] and is contained below for convenience. The symmetric 2nd rank tensors, like the heat conduction tensor κ_{ij}, the diffusion tensor D_{ij}, the thermodiffusion tensor D^T_{ij}, and magnetic relaxation tensor b^D_{ij}, have 3 independent coefficients

$$\kappa_{ij} = \kappa_{\parallel}\, n_i n_j + \kappa_{\perp}\delta^3_{ij} + \kappa_3 m_i m_j \tag{4.49}$$

where $\delta^3_{ij} = \delta_{ij} - n_i n_j - m_i m_j$.

For the third order tensors

$$c^D_{ijk} = c^D_1\left(\epsilon_{imk}n_m n_j + \epsilon_{imj}n_m n_k\right) + c^D_2\left(\epsilon_{imk}m_m m_j + \epsilon_{imj}m_m m_k\right) \tag{4.50}$$

$$\lambda_{ijk} = \lambda_1(\delta^3_{ij}n_k + \delta^3_{ik}n_j) + \lambda_2(m_i m_j n_k + m_i m_k n_j) \tag{4.51}$$

there is one coefficient more than in the uniaxial case, each. The orientational diffusion and relaxation of the director is governed by 1 coefficient each (cf. eq.(4.27))

$$R = \frac{1}{2}(\frac{1}{\gamma_0}\delta^3_{ij} + \frac{1}{\gamma_3}m_i m_j)h^n_i h^n_j + \ldots \tag{4.52}$$

and the viscosity tensor has four additional coefficients

$$\begin{aligned}\nu_{ijkl} = {} & \nu_1 m_i m_j m_k m_l + \nu_2 n_i n_j n_k n_l + \nu_3\delta^3_{ij}\delta^3_{kl} + \nu_4\left(m_k m_l n_i n_j + m_i m_j n_k n_l\right)\\ & +\nu_5\left(m_k m_l\delta^3_{ij} + m_i m_j\delta^3_{kl}\right) + \nu_6\left(n_k n_l\delta^3_{ij} + n_i n_j\delta^3_{kl}\right)\\ & +\nu_7\left(m_j m_l n_i n_k + m_j m_k n_i n_l + m_i m_k n_j n_l + m_i m_l n_j n_k\right)\\ & +\nu_8\left(m_j m_l\delta^3_{ik} + m_j m_k\delta^3_{il} + m_i m_k\delta^3_{jl} + m_i m_l\delta^3_{jk}\right)\\ & +\nu_9\left(n_j n_l\delta^3_{ik} + n_j n_k\delta^3_{il} + n_i n_k\delta^3_{jl} + n_i n_l\delta^3_{jk}\right)\end{aligned} \tag{4.53}$$

The reversible dynamic coupling between director and magnetization is still given by only one coefficient χ^R (4.24, 4.25), but now contains only the out-of-plane components $Y^R_i m_i$ or $h^n_i m_i$ and $X^R_i\delta^3_{ij}$ or $h^M_i\delta^3_{ij}$.

In the biaxial case some new additional terms cubic in $\boldsymbol{M}$ can be produced in (3.25, 3.36, 4.26, 4.33) by replacing any pair $n_i n_j$ with $M_i M_j$, e.g. δ^{tr}_{ij} by $\delta^3_{ij} = \delta_{ij} - n_i n_j - M_i M_j$ and $M_i M_j$ terms.

4.7 Summary

In this chapter we derive the complete set of macroscopic dynamic equations for ferronematics introducing the magnetization as an independent slowly relaxing variable. We show that orientational changes of the magnetization are coupled to nematic director reorientations not only in the statics, but in the dynamics as well. In addition, there are reversible and dissipative dynamic cross-couplings between (compressional, shear and elongational) flow, (rotations and

changes of the absolute value of the) magnetization and director reorientations. Some of these couplings are only possible, when a finite magnetization is present due to spontaneous magnetic order and/or due to an external magnetic field. In order to measure some combinations of the parameters that describe these cross-couplings we study the sound wave spectrum and the rheology of shear flow. There is an additional field dependent contribution to sound damping due to such a cross-coupling. For the case of a sound wave propagating in a direction oblique to the preferred directions (set by equilibrium magnetization, nematic director, or perpendicular to them) compressional flow (and changes of the absolute value of the magnetization) are coupled to shear flow (and rotations of the director and the magnetization). In addition we discussed the linear response of the system to oscillatory shear flow concentrating on frequencies below the transverse magnetization relaxation frequency. This allows to describe the influence of the magnetic dynamic degree of freedom on the nematic director diffusion/relaxation mode for ferronematic systems and the influence of the magnetic field on it. Even without a magnetic field the apparent viscosity is different from the bare one and the modified nematic director diffusion couples to the flow response. In the presence of an external field the director diffusion/relaxation is shifted to a finite frequency, which approximately increases with the third power of the field strength. Even in the field-free case there are shear-flow-induced oscillations of the magnetization out of the shear plane.

Chapter 5

Macroscopic dynamics of ferrogels

5.1 Introduction

In this chapter we generalize the set of hydrodynamic equations for ordinary gels to those for ferrogels by including the magnetization as an additional, slowly relaxing variable. The relaxation of the magnetization is rather slow compared to the (many) microscopic relaxation processes and it is therefore reasonable to keep the magnetization as a macroscopic, slowly relaxing variable.

We assume in our model that the magnetic particles are "attached" to the network, although the precise meaning of that is unclear on the molecular level. On the macroscopic level this leads to a coupling of rotations of the magnetization as well as changes of its absolute value with the elastic strains or stresses. As an application for these equations we discuss the spectrum of longitudinal and transverse sound in the presence of an external magnetic field. In the low frequency limit a comparison with static elastic measurements is made. A possible way of exciting shear waves by oscillating temperature gradients in the presence of a gradient field is outlined.

5.2 Statics and Thermodynamics

The macroscopic description of a system starts with the identification of the relevant variables. Apart from the quantities that are related to local conservation laws, like mass density (ρ), momentum density ($\boldsymbol{g}$), energy density (ε) and concentration (c) of the swelling fluid (and/or that of the magnetic particles), we consider the elastic strain u_{ij} and the magnetization $\boldsymbol{M}$ as additional variables. In a crystal the former is related to the broken translational symmetry due the long range positional order, which gives rise to the displacement vector $\boldsymbol{u}$ as a hydrodynamic symmetry variable. Since neither solid body translations nor rigid rotations give rise to elastic deformations, the strain tensor is used as variable, which reads in linearized version $u_{ij} = \frac{1}{2}\left(\nabla_i u_j + \nabla_j u_i\right)$ in. In amorphous solids, like rubbers, gels etc., linear elasticity is still described by a second rank, symmetric strain tensor. For a proper description of nonlinear elasticity cf. [46]. For the purpose of this work, however, linear elasticity is sufficient. As discussed in the Introduction the magnetization $\boldsymbol{M}$ is a slowly relaxing variable in the superparamagnetic case.

Assuming local thermodynamic equilibrium, i.e. all microscopic, fast relaxing quantities are already in equilibrium, we have the Gibbs relation

$$d\varepsilon = Td\sigma + \mu d\rho + \mu_c dc + v_i dg_i + H_i dB_i + h_i^M dM_i + \Psi_{ij} du_{ij}. \tag{5.1}$$

relating all macroscopically relevant variables discussed above to the entropy density σ. $\boldsymbol{B}$ is the magnetic induction field included here in order to accommodate the static Maxwell equations. In eq.(5.1) the thermodynamic quantities, chemical potential (μ), temperature (T), relative chemical potential (μ_c), velocity (v_i), elastic stress (Ψ_{ij}), magnetic field (H_i), and the magnetic molecular field (h_i^M), are defined as partial derivatives of the energy density with the respect to the appropriate variables [34].

To determine these thermodynamic forces and thus the static properties of magnetic elastomers one provides an expression of the energy density in terms of the variables

$$\begin{aligned} \varepsilon &= \varepsilon_0 + \frac{B^2}{2} - \boldsymbol{B}M + \frac{\mu_{ijkl}}{2} u_{ij}u_{kl} - \frac{\gamma_{ijkl}}{2} M_i M_j u_{kl} + \frac{\alpha}{2} M_i^2 + \frac{\beta}{4}\left(M_i^2\right)^2 \\ &\quad + u_{ii}\left(\chi^\rho \delta\rho + \chi^\sigma \delta\sigma + \chi^c \delta c\right) \end{aligned} \tag{5.2}$$

where ε_0 is the energy density of a fluid binary mixture. eq.(5.2) explicitly contains the elastic and the magnetic energy, their crosscoupling (the magneto-elastic energy) and bilinear couplings of compression with the scalar variables. To discuss large elastic deformations (rubber elasticity) one should keep terms of higher order of u_{ij}, which are neglected here. The magneto-elastic coupling is cubic [37] and the $\boldsymbol{M}^4$ contribution is kept in order to guarantee the thermodynamic stability. The tensors μ_{ijkl} and γ_{ijkl} take the isotropic form $a_{ijkl} = a_1\delta_{ij}\delta_{kl} + a_2\left(\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk} - \frac{2}{3}\delta_{ij}\delta_{kl}\right)$, where μ_1 is the compressibility and μ_2 the shear modulus. The magneto-elastic energy is similar to that for ferromagnetic materials, where however the compressional magnetostriction is neglected ($\gamma_1 = 0$) [37]. We will not take this approximation for magnetic gels and keep $\gamma_1 \neq 0$, in order to explore effects due to a non-zero γ_1 and how they can be measured. While γ_1 describes the elastic response to changing the field strength (or vice versa compression or dilation due to changes in $|\boldsymbol{M}|$), γ_2 is related to elastic shear and to rotations of $\boldsymbol{M}$. Depending on how the "attachment" of the magnetic clusters to the network actually is realized in a sample, this interaction may be large or small. Thus measuring the γ's by their effects described below, may give some hints on the microscopic structures. All static susceptibilities, like the elastic and magneto-elastic moduli as well as those describing crosscouplings between compression and the density, entropy density, and concentrations variations (χ^ρ, χ^σ and χ^c, respectively) can depend on $\boldsymbol{M}^2$ and thus on magnetic field strength..

Using eqs.(5.1,5.2), the magnetic Maxwell field H_i is defined in the usual way

$$H_i = \left(\frac{\partial\varepsilon}{\partial B_i}\right)_{\boldsymbol{M},u_{ij},\ldots} = B_i - M_i, \tag{5.3}$$

while the magnetic molecular field h_i^M reads

$$h_i^M = \left(\frac{\partial\varepsilon}{\partial M_i}\right)_{\boldsymbol{B},u_{ij},\ldots} = -B_i - \gamma_{ijkl}M_j u_{kl} + \alpha M_i + \beta M^2 M_i \tag{5.4}$$

Note that because of the definition (5.3), it is not possible to have a direct coupling between the external field $\boldsymbol{B}$ and the strain; the deformation of the network is mediated by the magnetization via the coupling terms $\sim \gamma_{ijkl}$.

The elastic stress Ψ_{ij} has the following form

$$\Psi_{ij} = \left(\frac{\partial \varepsilon}{\partial u_{ij}}\right)_{\boldsymbol{M},\boldsymbol{B},\ldots} = \mu_{ijkl} u_{kl} - \frac{\gamma_{ijkl}}{2} M_k M_l + \delta_{ij}\left(\chi^{\rho}\delta\rho + \chi^{\sigma}\delta\sigma + \chi^{c}\delta c\right) \tag{5.5}$$

and depends on the magnetization.

5.3 Equilibrium

In equilibrium, both the elastic strain eq.(5.5) and the magnetic molecular field eq.(5.4) have to be zero. Without an external field or external strain there is no magnetization and no strain in equilibrium. A finite external field, taken along the $z-$ axis, $\boldsymbol{B} = B_0 \boldsymbol{e}_z$, induces an equilibrium magnetization ($\boldsymbol{M}^0 = M_0 \boldsymbol{e}_z$) and an non-zero strain (u^0_{ij}) due to the magnetostriction effect. Neglecting the couplings of density[1], entropy and concentration to the strain tensor we have

$$\Psi_{ij} = \left(\left(\mu_1 - \frac{2}{3}\mu_2\right) u^0_{kk} - \left(\frac{\gamma_1}{2} - \frac{\gamma_2}{3}\right) M_0^2\right)\delta_{ij} - \gamma_2 M^0_i M^0_j + 2\mu_2 u^0_{ij} = 0 \tag{5.6}$$

$$h^M_i = -B_0\delta_{iz} - \left(\gamma_1 - \frac{2}{3}\gamma_2\right) M^0_i u^0_{kk} - 2\gamma_2 M^0_j u^0_{ij} + \alpha M^0_i + \beta M_0^2 M^0_i = 0 \tag{5.7}$$

From $h^M_x = 0$, $h^M_y = 0$ and $\Psi_{xy} = 0$ it follows that $u^0_{xz} = 0$, $u^0_{yz} = 0$, and $u^0_{xy} = 0$ accordingly. The remaining conditions give

$$u^0_{xx} = u^0_{yy} = \frac{\mu_2\gamma_1 - \mu_1\gamma_2}{6\mu_1\mu_2} M_0^2 \tag{5.8}$$

$$u^0_{zz} = \frac{\mu_2\gamma_1 + 2\mu_1\gamma_2}{6\mu_1\mu_2} M_0^2 \tag{5.9}$$

leading to the volume change $U^0 \equiv u^0_{xx} + u^0_{yy} + u^0_{zz} = \frac{\gamma_1}{2\mu_1} M_0^2$. The magnetostrictive volume change of the ferrogel is determined by the bulk modulus μ_1 and by the coefficient γ_1, which couples the trace of the stress tensor to the magnitude of the magnetization.

From $h^M_z = 0$ we get implicitly the equilibrium magnetization as a function of the field $B_0 = M_0\left(\alpha + \beta M_0^2 - \left(3\gamma_1^2\mu_2 + 4\gamma_2^2\mu_1\right) M_0^2/\left(6\mu_1\mu_2\right)\right)$. Writing this relation in the form $\chi B_0 = (1+\chi)M_0$, a field-dependent magnetic susceptibility χ results with

$$\frac{1+\chi}{\chi} = \alpha + \left(\beta - \frac{3\gamma_1^2\mu_2 + 4\gamma_2^2\mu_1}{6\mu_1\mu_2}\right)\left(\frac{\chi B_0}{1+\chi}\right)^2 . \tag{5.10}$$

[1] A non-zero χ^{ρ} merely renormalizes γ_1 into $\gamma_1(1 - 3\kappa_s(\rho\chi^{\rho})^2)$, where κ_s is the compressibility.

The explicit form of eq.(5.10) follows from the (truncated) expansion (5.2) and is suitable for small external fields only. For high field intensities, when the magnetization reaches its saturation value, χ in eq.(5.10) has to be replaced by a more complicated function $\chi_0 = \chi(B_0)$, either measured [47] or calculated from reliable microscopic models. For the small deviations from equilibrium, which we are dealing with in the following, the simple form $\chi B_0 = M_0$ is sufficient for any field strength, when for χ the appropriate equilibrium value χ_0 is taken.

5.4 Dynamics

The hydrodynamic equations for conserved and slowly relaxing variables as well as for those associated with spontaneously broken continuous symmetries are

$$\frac{\partial}{\partial t}\rho + div\,\rho\boldsymbol{v} = 0 \tag{5.11}$$

$$\frac{\partial}{\partial t}\sigma + div\,\sigma\boldsymbol{v} + div\boldsymbol{j}^{\boldsymbol{\sigma}} = \frac{R}{T} \tag{5.12}$$

$$\frac{\partial}{\partial t}g_i + \nabla_j\Big(v_j g_i + \delta_{ij}[p_0 + \boldsymbol{B}\cdot\boldsymbol{H}] + \sigma^0_{ij} + \sigma_{ij}\Big) = 0 \tag{5.13}$$

$$\Big(\frac{\partial}{\partial t} + v_k\nabla_k\Big)u_{ij} + Y_{ij} = 0 \tag{5.14}$$

$$\rho\Big(\frac{\partial}{\partial t} + v_j\nabla_j\Big)c + div\,\boldsymbol{j}^c = 0 \tag{5.15}$$

$$\Big(\frac{\partial}{\partial t} + v_j\nabla_j\Big)M_i + (\boldsymbol{M}\times\boldsymbol{\omega})_i + X_i = 0 \tag{5.16}$$

where $\omega_i = \frac{1}{2}\epsilon_{ijk}\nabla_j v_k$ is the vorticity and

$$\sigma^0_{ij} = -B_jH_i - \frac{1}{2}(M_jh^M_i - M_ih^M_j) + \Psi_{jk}u_{ki}. \tag{5.17}$$

Using the fact that the energy density eq.(5.1) has to be invariant under constant rotation [34] eq.(5.17) can be simplified as

$$\sigma^0_{ij} = -\frac{1}{2}\left(B_iH_j + B_jH_i\right) + \frac{1}{2}\left(\Psi_{jk}u_{ki} + \Psi_{ik}u_{kj}\right) \tag{5.18}$$

The last term in eq.(5.18) is nonlinear, but since there is a finite strain in an external field, it will enter linear deviations from that constrained equilibrium. The thermodynamic pressure p_0 is given by

$$p_0 = -\varepsilon + T\sigma + \mu\rho + \boldsymbol{g}\cdot\boldsymbol{v}. \tag{5.19}$$

j^σ is the entropy current, in eqs.(5.14)-(4.16) Y_{ij} and X_i are the quasi-currents of the variables associated with broken translational symmetry (network) and slowly relaxing magnetization. To guarantee rotational invariance of the dynamical equation for the strain field, one must require $Y_{ij} = Y_{ji}$. The source term R/T in the dynamic equation for the entropy density is

the entropy production. The second law of thermodynamics reads $R \geq 0$ for dissipative and reversible process respectively.

Since we are not dealing with electromagnetic effects, we can use the static Maxwell equations to determine $\boldsymbol{B}$

$$curl\boldsymbol{H} = curl\left(\boldsymbol{B} - \boldsymbol{M}\right) = 0, \qquad div\boldsymbol{B} = 0. \tag{5.20}$$

All the currents can be split into dissipative and into reversible ($R = 0$) and irreversible ($R \geq 0$) parts. Using general symmetry and invariance arguments and the fact, that a magnetic field changes sign under time reversal, we obtain the linear currents

$$\begin{aligned}
j_i^{\sigma R} &= -\kappa^R \varepsilon_{ijk} M_k \nabla_j T - D^{TR} \varepsilon_{ijk} M_k \nabla_j \mu_c + \xi^{TR} \varepsilon_{ijk} M_k \Psi_j && (5.21)\\
j_i^{cR} &= -D^R \varepsilon_{ijk} M_k \nabla_j \mu_c + D^{TR} \varepsilon_{ijk} M_k \nabla_j T + \xi^{cR} \varepsilon_{ijk} M_k \Psi_j && (5.22)\\
\sigma_{ij}^R &= -\Psi_{ij} - c_{kij}^R(M) h_k^M - \nu_{ijkl}^R(M) A_{kl} && (5.23)\\
Y_{ij}^R &= -A_{ij} + \frac{1}{2}\lambda^M \left(\nabla_i \left(\nabla \times h^M\right)_j + \nabla_j \left(\nabla \times h^M\right)_i\right) - && (5.24)\\
&- \frac{1}{2}\left(\nabla_i \left(\xi^R \varepsilon_{jkl} M_l \Psi_k + \xi^{TR} \varepsilon_{jkl} M_l \nabla_k T + \xi^{cR} \varepsilon_{jkl} M_l \nabla_k \mu_c\right) + (i \longleftrightarrow j)\right) \\
X_i^R &= b^R \varepsilon_{ijk} M_k h_j^M + \lambda^M \left(\nabla \times \Psi\right)_i - c_{ijk}^R(M) A_{jk} && (5.25)
\end{aligned}$$

with $A_{ij} = \frac{1}{2}\left(\nabla_i v_j + \nabla_j v_i\right)$ and $\Psi_i = \nabla_j \Psi_{ij} = \nabla_j \Psi_{ji}$. Again, nonlinear elastic contributions have been neglected. Due to the new degree of freedom (magnetization) there is an additional term in the stress quasi-current eq.(5.24) and a counter term in X_i^R, which describes a dynamic cross-coupling between magnetization and the network. It does not exist in ordinary elastomers nor in isotropic ferrofluids. Its impact on the sound spectrum will be explored in Sec.5.5.2. The new coefficient λ^M (reversible dynamic coupling between the magnetization and the strain tensor) gives a small effect in the dynamics of order $\sim k^4$. The reversible second rank magnetization-dependent material tensors, like the reversible analogue of heat conduction $\kappa^R \varepsilon_{ijk} M_k$, diffusion $\sim D^R$, thermodiffusion $\sim D^{TR}$, magnetization relaxation $\sim b^R$, and the reversible coupling terms between temperature, concentration and elasticity $\sim \xi^{TR}$, $\sim \xi^{cR}$, $\sim \xi^R$ are all of the same form. The magnetization-dependent tensors

$$\begin{aligned}
\nu_{ijkl}^R(M) &= \nu_7^R[\epsilon_{ikp}\delta_{jl} + \epsilon_{ilp}\delta_{jk} + \epsilon_{jlp}\delta_{ik} + \epsilon_{jkp}\delta_{il}]\, M_p && (5.26)\\
c_{ijk}^R(M) &= c_2^R(\delta_{ij} M_k + \delta_{ik} M_j) + c_3^R M_i \delta_{jk}
\end{aligned}$$

are odd functions of the magnetization.

To derive the dissipative contributions to the currents it is most convenient to start with the expression for dissipation function R. The dissipative currents are then obtained by taking variational derivatives with respect to one thermodynamic conjugate while keeping all others fixed. Expanding the dissipation function R up to second order in the thermodynamic forces we obtain

$$\begin{aligned}
R &= \frac{1}{2}\kappa\left(\nabla_i T\right)^2 + \frac{1}{2}\nu_{ijkl}^D A_{ij} A_{kl} + \frac{1}{2} D\left(\nabla_i \mu_c\right)^2 + \frac{b}{2}\left(h_i^M\right)^2 \\
&+ \frac{1}{2}\xi\left(\Psi_i\right)^2 + D^T\left(\nabla_j T\right)\left(\nabla_j \mu_c\right) + \Psi_i\left(\xi^T \nabla_i T + \xi^c \nabla_i \mu_c\right) && (5.27)
\end{aligned}$$

Here ν^D_{ijkl} is the viscosity tensor (and has the same form as the elastic tensor μ_{ijkl} defined above) and κ, D and D^T describe heat conduction, diffusion and thermodiffusion, respectively. The quantity b is the inverse magnetization relaxation and ξ the self diffusion constant of the strain field. The range of possible values of the coefficients in eq.(5.27) is restricted by the positivity of the entropy production.

We derive the dissipative parts of the currents by taking the variational derivative of the dissipation function with respect to the appropriate thermodynamic force

$$
\begin{aligned}
j_i^{\sigma D} &= -\kappa\nabla_i T - D^T\nabla_i\mu_c - \frac{1}{2}\xi^T\Psi_i && (5.28)\\
j_i^{cD} &= -D\nabla_i\mu_c - D^T\nabla_i T - \frac{1}{2}\xi^c\Psi_i && (5.29)\\
\sigma_{ij}^D &= -\nu^D_{ijkl}A_{kl} && (5.30)\\
Y_{ij}^D &= -\frac{1}{2}\left(\nabla_i\left(\xi\Psi_j + \xi^T\nabla_j T + \xi^c\nabla_j\mu_c\right) + (i \longleftrightarrow j)\right) && (5.31)\\
X_i^D &= bh_i^M && (5.32)
\end{aligned}
$$

5.5 Experiments

5.5.1 Static elongation and shear

In preparation for, and for comparison with, the sound spectrum we first discuss static elongational and shear deformations. We assume an external field (along the z axis) that gives a non-zero magnetization as well as a deformation in equilibrium. This state is then disturbed by an external deformation Δu_{ij} by some mechanical device. Due to the magnetostriction effect this gives also rise to a change in the magnetization. In the static limit the magnetic degree of freedom is still in equilibrium and the change of the magnetization can be obtained from the condition $h_i^M = 0$, eq.(5.4). The applied deformation gives, directly by Hooke's law, and indirectly by the change of the magnetization, an elastic stress. From eq.(5.5) we get

$$
\begin{aligned}
\Psi_{zz} &= (\mu'' - \chi_0\gamma''^2 M_0^2)\Delta u_{zz} + (\mu' - \chi_0\gamma'\gamma'' M_0^2)(\Delta u_{xx} + \Delta u_{yy}) && (5.33)\\
\Psi_{xx} &= (\mu'' - \chi_0\gamma'^2 M_0^2)\Delta u_{xx} + (\mu' - \chi_0\gamma'^2 M_0^2)\Delta u_{yy} + (\mu' - \chi_0\gamma'\gamma'' M_0^2)\Delta u_{zz} && (5.34)\\
\Psi_{zx} &= 2(\mu_2 - \chi_0\gamma_2^2 M_0^2)\Delta u_{zx} && (5.35)\\
\Psi_{xy} &= 2\mu_2\Delta u_{xy} && (5.36)
\end{aligned}
$$

for the elastic stresses. Apart from the elastic moduli ($\mu'' = \mu_1 + (4/3)\mu_2$ and $\mu' = \mu_1 - (2/3)\mu_2$), it contains M_0^2 corrections due to magnetostriction ($\gamma' = \gamma_1 - (2/3)\gamma_2$ and $\gamma'' = \gamma_1 + (4/3)\gamma_2$), except for deformations that do not affect the magnetization. Due to the compressibility κ_s, defined as $\kappa_s = \rho^2(\partial^2\varepsilon/\partial\rho^2)^{-1}$, the coefficient μ'' has to be replaced by $\mu' = 1/(\rho\kappa_s) + \mu''$ for the effective response to various external deformations in the stress tensor. Note that, even if the deformation does conserve the volume ($\Delta u_{xx} + \Delta u_{yy} + \Delta u_{zz} = 0$), the trace of the elastic stress tensor is not zero, but given by $\Psi_{kk} = -6\chi_0\gamma_1\gamma_2 M_0^2\Delta u_{zz}$. The formulas (5.33-5.36) are applicable for small strains only, since it is based on Hooke's law, while for larger strains deviations from this law due to rubber elasticity are to be expected.

5.5.2 Propagation of sound

Due to the presence of the permanent polymer network in ferrogels compared to ferrofluids, there are transverse as well as longitudinal sound eigenmodes. In this section we derive the longitudinal and the transverse sound of the system with an external magnetic field parallel to the $z-$ axis. We neglect all diffusional processes connected e.g. with viscosity and heat conduction as well as their reversible counterparts. Terms with λ^M- and b^R- coefficients are omitted here as well. The first one does not contribute to the sound velocity, because it is of fourth order in the wave vector $\sim k$. Terms with b^R shift the magnetization relaxation time by $\sim b^R M^2$, and thus give higher order corrections $\sim M^4$ to the sound spectrum, in which we are not interested here. Only the relaxation the magnetization in the field is kept.

Assuming a one-dimensional plane wave with space-time dependence $\sim \exp i(-\omega t + \boldsymbol{k}\cdot\boldsymbol{r})$ for all deviations δu_{ij}, δM_i, v_i, $\delta\rho$ from the equilibrium values determined in Sec.5.3 the linearized set of dynamic equations becomes an algebraic one. Let us consider sound in the two cases, where the external magnetic field and the equilibrium magnetization are either perpendicular or parallel to the wave vector. Field fluctuations δB_i are fixed by the static Maxwell equations (5.20) to $\delta B_i = \delta M_j(\delta_{ij} - k_i k_j k^{-2})$.

In the case where an external field is perpendicular to the wave vector the sound dispersion relations for longitudinal and for transverse modes, respectively, read, up to order $O(M^2)$ from here on all old μ' are called $\tilde{\mu}$

$$\omega_l^2 = \frac{k^2}{\rho}\left[\mu' - {M_0}^2\left(\mu'\frac{\mu_2\gamma_1 - \mu_1\gamma_2}{6\mu_2\mu_1} + \chi_0\left(\gamma'\right)^2 - \frac{\imath\omega\left(\chi_0\gamma' - c_3^R\right)^2}{\imath\omega\chi_0 - b}\right)\right] \tag{5.37}$$

$$\omega_{t1}^2 = \frac{k^2}{\rho}\left[\mu_2 - {M_0}^2\frac{\mu_2\gamma_1 - \mu_1\gamma_2}{6\mu_1}\right] \tag{5.38}$$

$$\omega_{t2}^2 = \frac{k^2}{\rho}\left[\mu_2 - {M_0}^2\left(\frac{2\mu_2\gamma_1 + \mu_1\gamma_2}{12\mu_1} + \chi_0\gamma_2^2 + \frac{\gamma_2}{2} - \frac{\imath\omega\left(\chi_0\gamma_2 - c_2^R + \frac{1}{2}\right)^2}{\imath\omega\chi_0 - b}\right)\right], \tag{5.39}$$

where $\mu' = 1/(\rho\kappa_s) + \mu_1 + \frac{4}{3}\mu_2$ and $\gamma' = \gamma_1 - \frac{2}{3}\gamma_2$. Generally, $\chi_0(B_0)$ brings in an additional dependence on M_0, which however can be neglected in $O(M^2)$.

If an external field is parallel to the wave vector we have the following longitudinal and transverse dispersion relations

$$\omega_l^2 = \frac{k^2}{\rho}\left[\mu' - {M_0}^2\left(\mu'\frac{\mu_2\gamma_1 + 2\mu_1\gamma_2}{6\mu_2\mu_1} + \chi_0\left(\gamma''\right)^2 - \frac{\imath\omega\left(\chi_0\gamma'' - \left(2c_2^R + c_3^R\right)\right)^2}{\imath\omega\chi_0 - b}\right)\right] \tag{5.40}$$

$$\omega_t^2 = \frac{k^2}{\rho}\left[\mu_2 - {M_0}^2\left(\frac{2\mu_2\gamma_1 + \mu_1\gamma_2}{12\mu_1} + \chi_0\gamma_2^2 - \frac{\gamma_2}{2} - \frac{\imath\omega\left(\chi_0\gamma_2 - c_2^R - \frac{1}{2}\right)^2}{\imath\omega\chi_0 - b}\right)\right], \tag{5.41}$$

where $\gamma'' = \gamma_1 + \frac{4}{3}\gamma_2$. As the problem is symmetric in the plane perpendicular to the magnetic field the two transverse sounds have identical dispersion relations.

Knowing the dispersion relations for the two geometries one can study sound velocities. The relaxation time of the magnetization $\tau_M = \chi_0/b$ is known for ferrofluids and is typically of order 10^{-4}. Our approach allows to investigate two frequency regimes: for $\omega < 1/\tau_M$ the low frequency limit and for $\omega > 1/\tau_M$ the high frequency regime. There is no frequency dependence

for the transverse sound mode, where the magnetic field, the wave vector and the velocity are mutually perpendicular, eq.(5.38).

Let us first investigate low frequencies ($\omega < 1/\tau_M$). The frequency-dependent parts in the square brackets of the dispersion relations (5.37-5.41) become dissipative and do not contribute to the sound velocities. In the case of the external field being perpendicular to the wave vector the velocities of the longitudinal c_l and the transverse sounds c_{t1}, c_{t2} read

$$c_l^2 = \frac{\tilde{\mu}}{\rho} - \left(\tilde{\mu} \frac{\mu_2\gamma_1 - \mu_1\gamma_2}{6\rho\mu_2\mu_1} + \frac{\chi_0 \left(\gamma'\right)^2}{\rho} \right) M_0^2 \tag{5.42}$$

$$c_{t1}^2 = \frac{\mu_2}{\rho} - \left(\frac{\mu_2\gamma_1 - \mu_1\gamma_2}{6\rho\mu_1} \right) M_0^2 \tag{5.43}$$

$$c_{t2}^2 = \frac{\mu_2}{\rho} - \left(\frac{2\mu_2\gamma_1 + \mu_1\gamma_2}{12\rho\mu_1} + \frac{2\chi_0\gamma_2^2 + \gamma_2}{2\rho} \right) M_0^2 \tag{5.44}$$

while for a parallel field we have

$$c_l^2 = \frac{\mu'}{\rho} - \left(\mu' \frac{\mu_2\gamma_1 + 2\mu_1\gamma_2}{6\rho\mu_1\mu_2} + \frac{\chi_0 \left(\gamma''\right)^2}{\rho} \right) M_0^2 \tag{5.45}$$

$$c_t^2 = \frac{\mu_2}{\rho} - \left(\frac{2\mu_2\gamma_1 + \mu_1\gamma_2}{12\rho\mu_1} + \frac{2\chi_0\gamma_2^2 - \gamma_2}{2\rho} \right) M_0^2 \tag{5.46}$$

The sound speeds at low frequencies and zero field give information about the compressibility and the elastic moduli (bulk and shear). The dependence on M_0^2 is due to magnetostrictive effect and completely absent for $\gamma_1 = 0 = \gamma_2$. Magnetostriction enters the sound speed in different ways. There is a direct static coupling of magnetization and stress in eq.(5.5) and the strain dependence of the magnetic molecular field (5.4), which give rise to terms linear and quadratic in γ_1 and γ_2. A similar term emerges indirectly via the Maxwell stress. The second route is dynamic, given by the nonlinear elastic stress contribution to the stress tensor in eq.(5.18), which however is effectively linear due to the non-zero equilibrium strains. In the sound speeds these contributions are of the bilinear $\gamma\mu$ type. In an external field the effective moduli measured by sound propagation are therefore different from those measured by static elongational or shear deformation measurements discussed in the preceding subsection. The coincidence of static elasticity and low frequency sound speed is restored in the limit of vanishing magnetic field only, when in both cases deviations from the *true* thermodynamic equilibrium are considered.

The sound velocities change with an external magnetic field basically with the second power of the field, which is in accordance with experiments on longitudinal sound [47]. There is, however, an additional field dependence through χ_0. Whether the sound velocities are decreased or increased by the field cannot be established by general rules, since the signs of $\gamma_{1,2}$ are not fixed and can be material dependent. Measurements of transverse and longitudinal sound velocities in the different geometries will provide informations on the magnitude and sign of the magnetostrictive and elastic moduli. As a first approximation the magnetostrictive volume change ($\sim \gamma_1 M_0^2/\mu_1$) can be neglected in those rubbers and only shape changes remain.

Damping of sound waves generally is rather weak and given by the imaginary part of the dispersion relation. In addition to the usual magnetic-field independent sound damping due to

viscosity and other diffusional processes there is a field-dependent sound damping in ferrogels. This is an effect of the reversible, dynamic coupling of the magnetization to flow, either phenomenological ($c^R_{ijk}(M)$ in (5.25)) or kinematic ($\epsilon_{ijk}M_j\omega_k$ in (5.16)) and its counterparts in the Navier-Stokes equation. For example, when the magnetic field is parallel (perpendicular) to the wave vector a field-dependent damping of longitudinal (transverse) sound eq.(5.40) (eq.(5.39)) reads, respectively

$$\mathfrak{Im}(\omega_l) = -\frac{1}{2}\frac{\left(\chi_0\gamma'' - \left(2c_2^R + c_3^R\right)\right)^2}{\rho b}M_0^2k^2 \tag{5.47}$$

$$\mathfrak{Im}(\omega_{t2}) = -\frac{1}{2}\frac{\left(\chi_0\gamma_2 - c_2^R + \frac{1}{2}\right)^2}{\rho b}M_0^2k^2 \tag{5.48}$$

the first of which can be related to the observed increase of the apparent viscosity due to the magnetic field [48]. In all cases $\mathfrak{Im} < 0$, as it should be according to the second law of thermodynamics.

Let us now investigate the high frequency limit for $\omega > 1/\tau_M$. In the case where an external field is perpendicular to the wave vector the velocities of the longitudinal c_l and the transverse sounds c_{t2} read (c_{t1} is as in the low frequency limit)

$$c_l^2 = \frac{\mu'}{\rho} - \left(\mu'\frac{\mu_2\gamma_1 - \mu_1\gamma_2}{6\rho\mu_2\mu_1} + \frac{c_3^R\left(2\chi_0\gamma' - c_3^R\right)}{\chi_0\rho}\right)M_0^2 \tag{5.49}$$

$$c_{t2}^2 = \frac{\mu_2}{\rho} - \left(\frac{2\mu_2\gamma_1 + \mu_1\gamma_2}{12\rho\mu_1} + \frac{2\chi_0\gamma_2\left(c_2^R - \frac{1}{4}\right) - \left(c_2^R - \frac{1}{2}\right)^2}{\chi_0\rho}\right)M_0^2 \tag{5.50}$$

For an external field parallel to the wave vector we have

$$c_l^2 = \frac{\tilde{\mu}}{\rho} - \left(\tilde{\mu}\frac{\mu_2\gamma_1 + 2\mu_1\gamma_2}{6\mu_2\mu_1\rho} + \frac{\left(2c_1^R + c_2^R\right)\left(2\chi_0\gamma'' - \left(2c_1^R + c_2^R\right)\right)}{\chi_0\rho}\right)M_0^2 \tag{5.51}$$

$$c_t^2 = \frac{\mu_2}{\rho} - \left(\frac{2\mu_2\gamma_1 + \mu_1\gamma_2}{12\mu_1\rho} + \frac{2\chi_0\gamma_2(c_1^R + \frac{1}{4}) - \left(c_1^R + \frac{1}{2}\right)^2}{\chi_0\rho}\right)M_0^2 \tag{5.52}$$

The field dependence of the sound velocities contains the magnetostrictive contributions already present in the low frequency limit, but in addition also the reversible, dynamic crosscouplings (c_2^R, c_3^R) between magnetization and flow (which in the low frequency limit contributed to the sound damping). Of course, most interesting experimentally is the transition region $\omega\tau_M \approx 1$, where the sound velocities make steps and the damping is enhanced.

5.5.3 Shear excitation by temperature oscillations

In ferrogels there are several reversible crosscouplings mediated by material tensors that are linear in the external magnetic field. They belong to the same type of effects as the Hall and the Righi-Leduc effect. In eq.(5.24) there is such a coupling, described by ξ^{TR}, between a

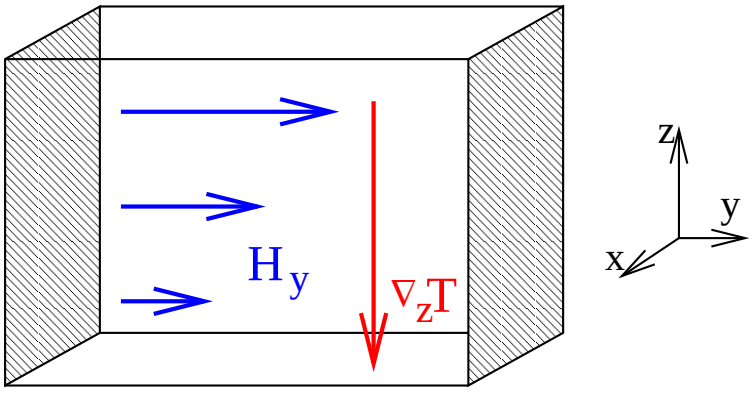

Figure 5.1: Shear excitation u_{xz} in a ferrogel due to applied temperature oscillations along the z-direction, in the presence of a constant or gradient magnetic field in y-direction.

temperature gradient and the dynamics of the elastic degree of freedom. From the form of ξ^{TR} one can conclude that an applied oscillating temperature $T = T_0 + T_1 exp[i(kz - \omega t)]$, in the presence of a homogeneous or gradient magnetic field [2] $\boldsymbol{H} = \hat{\boldsymbol{e}}_y(H_0 + H_1 z)$, leads to an oscillating shear in the plane perpendicular to the magnetic field (Fig.5.5.3), since $Y_{xz} \sim a \equiv \frac{1}{2}\chi_0 \xi^{TR} T_1 (H_1 + ikH_0)$. Oscillating shear u_{xz} is part of the transverse sound discussed in the previous subsection. After the initial transients have died out the excited shear wave travels with the frequency and wave vector of the applied temperature, $u_{xz} = u_0\, exp[i(kz - \omega t)]$, with the complex amplitude u_0 given by

$$\left(-i\omega - \frac{c_{t1}^2 k^2}{i\omega - \frac{\nu}{\rho}k^2} + \xi\mu_2 k^2 \right) u_0 = ika \tag{5.53}$$

where c_{t1} is the shear wave velocity (5.43), ν the shear viscosity, and ξ the self diffusion of the strain field (5.31). The former comprises a field dependent part, which is space dependent in a gradient field. However, that part is small compared to the constant one (μ_2/ρ) and can be approximated by its spatial mean or can be neglected at all here. If the ratio ω/k for the applied temperature is in the range of the transverse sound velocity, we have $\omega \gg (\nu/\rho)k^2$ and $\omega \gg \xi\mu_2 k^2$, and (5.53) gives the amplitude of the excited shear wave in the long time limit in the form of a response of a damped harmonic oscillator

$$u_0 = \frac{-ak\omega}{\omega_0^2 - \omega^2 + 2i\omega\Gamma} \tag{5.54}$$

with eigenfrequency $\omega_0 = c_{t1}k$ and damping $2\Gamma = k^2(\xi\mu_2 + \nu/\rho)$.

The real part of the strain tensor, which is the measurable quantity, has the form

$$\mathfrak{Re}\,(u_{xz}) = A_{1,2}\cos\left(kz - \omega t + \delta_{1,2}\right) \tag{5.55}$$

where $A_{1,2} = a_{1,2}\, k\omega \left(\left(\omega_0^2 - \omega^2\right)^2 + 4\omega^2\Gamma^2 \right)^{-1/2}$ and $\delta_2 = \delta$, $\delta_1 = \delta - \pi/2$ with $\tan\delta = \left(\omega^2 - \omega_0^2\right)/\left(2\omega\Gamma\right)$ for the two cases of a constant magnetic field $a_2 = \frac{1}{2}\chi_0 \xi^{TR} T_1 k H_0$, and a

[2] The field component $\hat{\boldsymbol{e}}_z H_1 y$, present due to $curl\,\boldsymbol{H} = 0$, does not contribute.

field gradient $a_1 = \frac{1}{2}\chi_0 \xi^{TR} T_1 H_1$, respectively. This reduces to

$$u_{xz} = \frac{a_1 k}{2\Gamma} \sin(kz - \omega_0 t) \qquad \text{or} \qquad u_{xz} = \frac{a_2 k}{2\Gamma} \cos(kz - \omega_0 t) \tag{5.56}$$

in the resonant cases $\omega = \omega_0$. Of course, this coupling of temperature to shear also works the other way round, and an imposed shear wave can excite a temperature wave in the presence of an appropriate magnetic field (gradient).

Another possibility of shear excitation is the application of concentration instead of a temperature oscillations (see eq.(5.24)), although this might be more challenging experimentally.

5.6 Summary

In this chapter we have given the hydrodynamic equations for magnetic elastomers including the magnetization as an independent slowly relaxing variable, which allows to study the system for high frequencies as well. Due to presence of the permanent network the displacement field $\mathbf{u}$ is a truly hydrodynamic variable. The fact, that magnetic grains are "attached" to the network is expressed by the static coupling of the magnetization and the strain tensor. This leads to an additional field dependent contribution to the sound spectrum. The contribution to the transverse sound modes depends on the relative angle between an external field and the wave vector. From the low frequency limit of the sound spectrum one can obtain information about the effective, magnetic field dependent elastic moduli. However, these moduli are different from those measured by static elongations or shear deformations in an external field. The reason is that due to the finite magnetostriction the linear response theory is not applicable. Only in the limit of a vanishing field they are equal and match the true elastic moduli. In the high frequency limit one gets a shift in the sound velocities proportional to the dynamic coupling between the flow and the magnetization. This reflects the fact, that the magnetization is an independent variable. Finally, a shear excitation experiment in an oscillating temperature gradient plus a gradient of the magnetic field has been proposed.

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